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OZONE

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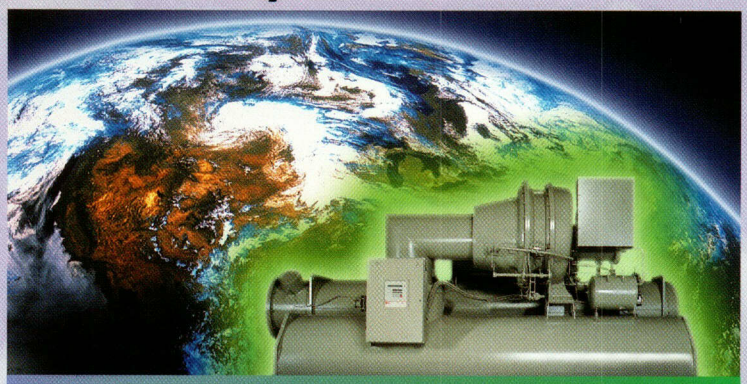
CONFERENCE PROCEEDINGS

Announcing

.48 kW/Ton in '98



TRANE EARTH•WISE™ CENTRAVAC®

The World's Most Efficient, Lowest Emissions Chiller

The Trane Earth•Wise CenTraVac has a proven track record as literally the world's most efficient, lowest emissions chiller. However, with this announcement that leadership grows. In 1998 a significant portion of the product line will be selectable at an unmatched efficiency level of .48kW/ton, at standard ARI rated conditions. And this builds on the successful 1997 introduction of .49 kW/ton across the entire product line, from 300 to nearly 2500 tons.

This is an efficiency level of 16 to 25 percent better than competitive chillers using other alternative refrigerants, which are typically in the .56 to .60 kW/ton range. And, at part-load conditions, the kW/ton ratings are even better; a fact that can be seen by comparing Trane's ARI certified applied part load values (APLV's) to those of competitive units.

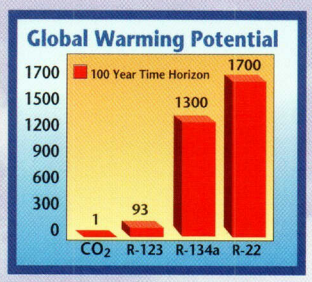
Business-Wise...

For a 1000-ton chiller, this efficiency difference can provide savings of over $24,000 per year or nearly three quarters of a million dollars over the life of the machine... typically more than twice the initial cost of the machine.

And Earth•Wise

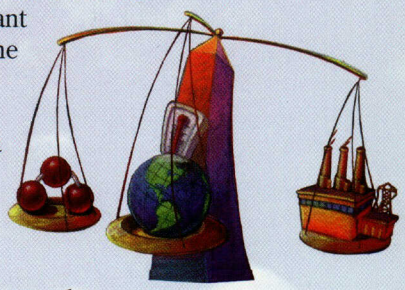
The development of the .48 kW/ton chiller also has a positive environmental impact. Consider this: If every centrifugal chiller in the world were able to operate at .48 vs .56 kW/ton, utility generated greenhouse gas emissions could be reduced annually by nearly 17 billion pounds of CO_2 while SO_2 and NO_x could be reduced by over 64 and 27 billion grams, respectively. This reduction is equivalent to removing more than two million cars from the road or to planting nearly 500 million trees each year.

Furthermore, the Trane "near zero" emissions Earth•Wise chiller also has the lowest total refrigerant emissions in the industry. So low that it's essentially a closed system.



The key to the industry's highest energy efficiency and lowest leak rate is the use of a low pressure refrigerant DuPont calls SUVA-123; a refrigerant that has the lowest direct-effect global warming potential and the highest thermodynamic efficiency of all non-CFC refrigerants; a refrigerant in use in more new centrifugals today than all other alternatives combined.

The Future Is In The Balance



Reduced power plant emissions and the industry's lowest refrigerant emission rate put the Trane .48 kW/ton Earth•Wise centrifugal chiller in a class by itself, from both a business and an environmental standpoint. The future lies in the prudent balance that takes into account the importance of ozone depletion, global warming and energy efficiency. A balance that is right for both business and the environment.

How do you design a centrifugal chiller to be up to 25 percent more efficient with near zero emissions? A new "Refrigerant Issues Update" video provides an insightful answer to this question and more. For a free CFC-VID-26, contact your local Trane commercial sales office.

TRANE

Creating The Right Atmosphere®

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Thermodynamic Properties and Cycle Performance of a New Alternative Refrigerant, HFE-245mc

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Abstract

Since HFE-245mc has both lower ozone depletion potential (ODP) and smaller global warming potential (GWP), it is expected being a possible candidate to replace R-114, especially for its high temperature heat-pump applications. We report a complete set of vapor pressures and *PVT* properties of HFE-245mc measured by a constant volume method. One hundred and ten vapor pressures were obtained from 310 K to the critical temperature (406.80 K) and a vapor pressure correlation has been developed. One hundred and twenty-four *PVT* property data in the range of temperatures from 360 K to 440 K and pressures up to 8.4 MPa were also obtained along 12 isochores. A virial-expansion type equation of state to represent the present measurements has also been developed. On the basis of the present measurements and formulations, its applicability to the vapor–compression heat-pump systems has been discussed by evaluating the cycle performance in the present paper.

Introduction

In accord with an increasing concern about the global warming issue, even HFC (hydrofluorocarbon) alternative refrigerants to replace conventional HCFC (hydrochloro-fluorocarbon) refrigerants are currently considered not being a long-term substitute, as a working fluid for air-conditioning, heat-pumping and refrigerating equipments throughout the forthcoming 21st century, although HFCs virtually have no potential to deplete the stratospheric ozone layer.

As one of Japanese national R&D projects, therefore, the New Energy and Industrial Technology Development Organization (NEDO) has been challenging, for the last several years, to search so-called "new generation refrigerants" which should have far lower GWP than HFCs. Among the candidates thus proposed recently [1] by the Research Institute of Innovative Technology for the Earth (RITE), there exists HFE-245mc (pentafluoroethyl methyl ether : $CF_3CF_2OCH_3$) as a promising candidate to replace R-114 especially for vapor-compression heat-pump system applications.

The present study aims to provide reliable thermodynamic property data on HFE-245mc and thermodynamic model to represent them so as to challenge such an application mentioned above. In addition, the basic evaluation of theoretical cycle performance of high temperature heat-pumping system with this new alternative refrigerant is discussed.

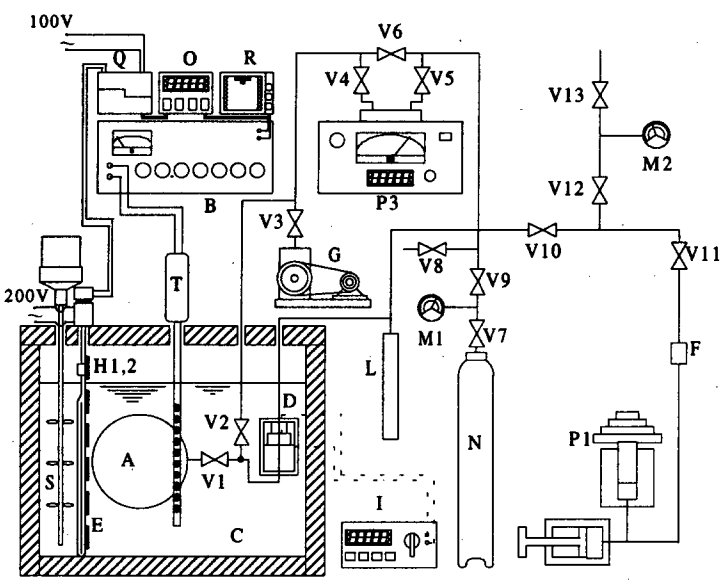
Literature Survey

There are two available literatures about the thermodynamic properties of HFE-245mc. Sako et al. [2] have measured vapor pressures and the critical temperature and pressure by observing the behavior of the interface between the vapor and liquid phase coexisting within an equilibrium cell thorough the glass window as for HFE-245mc and other 11 fluorinated ethers, and developed a four-term Wagner type vapor pressure correlations. Sako et al. [3] have also reported the critical parameters of HFE-245mc and other 6 fluorinated ethers by visual observation of the appearance and/or disappearance of the meniscus with the uncertainties of ±30 mK in the critical temperature, ±2.0 kPa in the critical pressure and ±0.2 % in the critical density, respectively.

Some general properties and characteristics of various fluorinated ethers including HFE-245mc have also been reported by Misaki and Sekiya [1] at the 1996 International Conference on Ozone Protection Technologies.

Experimental

In the present study, a constant volume apparatus shown in Fig. 1 has been used to measure the vapor pressures and *PVT* properties. This apparatus is similar to that used in our earlier studies for R-134a [4], R-123 [5], R-125 [6] and R-236ea [7] and its reliability has been well confirmed. A prescribed mass of the sample with research grade purity (99.9967 mol%) is confined into a spherical thick-walled sample-cell (A) made of stainless steel with about 139 cm^3 in its inner volume and it is installed in a thermostated fluid-bath (C).



[A] : Sample cell [B] : Thermometer bridge [C] : Thermostated bath [D] : Differential pressure indicator [E] : Partition plate [F] : Dust filter [G] : Vacuum pump [H1,2] : Main / Sub heater [I] : Digital resistance meter [J] : Pressure damper [M1,2] : Pressure gauges [N] : Nitrogen bottle [O] : PID controller [P1] : Air piston type pressure gauge [P2] : Bourdon-tube pressure gauge [Q] : Thyristor regulator [R] : Pen recorder [S] : Stirrer [T] : Platinum resistance thermometer [V1-13] : Valves

Figure 1. Schematic of experimental apparatus

The sample temperature is not detected directly but is considered being the same as that of heat transfer medium within the thermostated fluid-bath, since a series of measurements have been performed under a well-established thermal equilibrium condition between the sample and bath fluid. The temperature of bath fluid detected by a platinum resistance thermometer (T) is automatically controlled within ±2 mK of its fluctuation using a PID controller (O), and is measured with a thermometer bridge (B).

The sample pressure is then measured, with an aid of an air-piston pressure-gauge (P1), as that of nitrogen gas [supplied from its bottle (N)] which serves as a pressure transferring medium existing at the upper space of the stainless-steel membrane equipped in a differential pressure indicator (D).

The sample density, on the other hand, is determined on the basis of the sample mass weighed by a precision chemical balance within the estimated uncertainty of ±3 mg and the inner volume of the sample cell associated with required minor corrections owing to thermal expansion and hydrostatic pressure deformation.

The experimental uncertainties of the present measurements have been estimated on the basis of the ISO recommendation [8] associated with a coverage factor being 2. The expanded uncertainties of measurements are ±10 mK in temperature, ±1.4 kPa in pressure and ±0.07 % in density, respectively.

Results and Discussion

1. Vapor pressures

One hundred and ten vapor pressures have been obtained for temperatures from 310 K to the critical temperature, which correspond to pressures between 0.3 MPa and 2.9 MPa. Based on the obtained data, a three-term Wagner-type vapor-pressure correlation has been developed as:

$$\ln P_r = \frac{1}{T_r}(-7.8491086\tau + 1.4699487\,\tau^{1.4} - 3.6933492\tau^{3.0}) \tag{1}$$

where $P_r = P_s/P_c$, is the reduced vapor pressure of HFE-245mc, P_s and P_c are the vapor pressure and the critical pressure of HFE-245mc, respectively. $T_r = T/T_c$, is the reduced temperature and τ is defined as $\tau = 1-T_r$. The critical pressure was then obtained from eq. (1) as:

$$P_c = 2886.3 \pm 1.5 \text{ kPa} \tag{2}$$

which corresponds to $T_c = 406.80 \pm 0.03$ K reported by Sako et al. [3]. This critical pressure value agrees with Ref. [3] within the reported experimental uncertainty.

The average deviation between the present measurements and eq. (1) is 0.05 %, while the maximum deviation is 0.18 %. Figure 2 shows the comparison of the present measured data and vapor-pressure correlation reported by Sako et al. [2] with eq. (1). Most of the present measurements are well represented by eq. (1) within the absolute deviation of ±1.0 kPa. Vapor pressures calculated from the correlation proposed by Sako et al., however, are lower than eq. (1) for almost entire range of temperatures and absolute deviation amounts to −11.0 kPa at 406.74 K, the critical temperature reported earlier by Sako et al. [2].

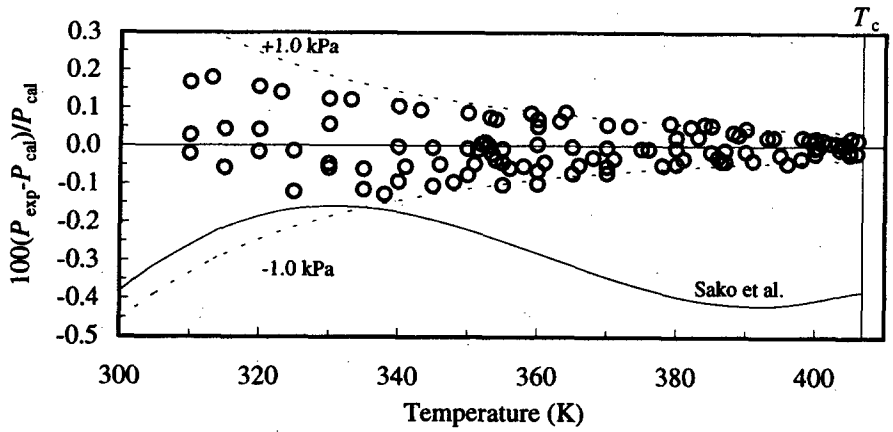


Figure 2. Vapor-pressure deviations of HFE-245mc from eq. (1)

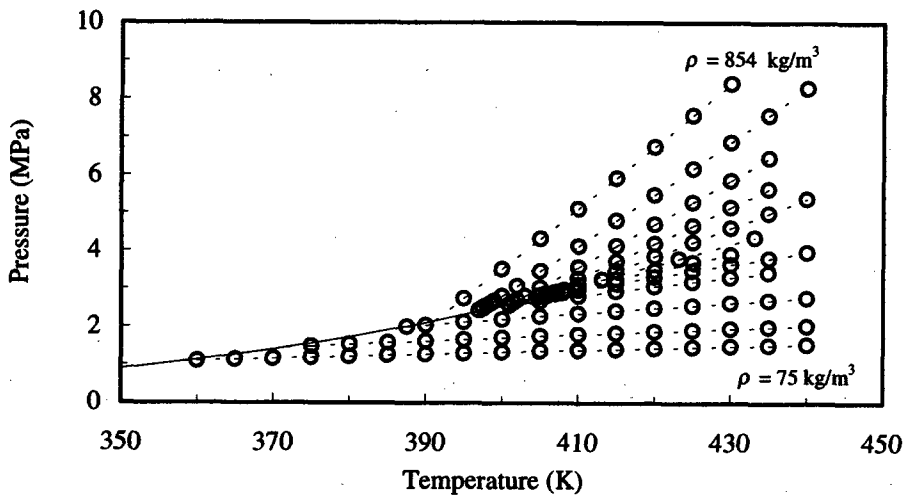


Figure 3. Distribution of experimental *PVT* data

2. *PVT* Properties

A total of 124 *PVT* properties of HFE-245mc have been measured along 12 different isochores covering an extensive range of temperatures 360-440 K, pressures 1.1-8.4 MPa and densities 75-854 kg/m^3 in the present study. A distribution of the present measurements is illustrated in Fig. 3 on a pressure-temperature diagram with our vapor-pressure curve calculated from eq. (1). All the *PVT* data have been used to fit a 14-coefficient virial-expansion type equation of state given below:

$$P_r = \frac{\rho_r T_r}{Z_c} + a_1 \exp\left(\frac{1}{T_r}\right)\rho_r^{\,2} + \sum_{i=2}^{14} a_i \rho_r^{\,\beta_i} T_r^{\,\alpha_i} \tag{3}$$

where, $P_r = P/P_c$, $T_r = T/T_c$, $\rho_r = \rho/\rho_c$, $Z_c = P_c/(\rho_c R T_c)$, $R = R_o/M$, and R_o and M are the universal gas constant and molar mass of HFE-245mc, respectively. The values of all the parameters and

numerical constants in eq. (3) are listed in Table 1. Pressure and density deviations of experimental *PVT* data from eq. (3) are shown in Fig.4 for different reduced densities. This model represents satisfactorily the present experimental data within ±0.3 % in pressure and within ±0.5 % in density deviation, respectively, for most of the present measurements. The developed equation of state is effective for the range of temperatures 350-450 K, pressures up to 9.0 MPa, and densities up to 900 kg/m^3.

Table 1. Numerical coefficients in eq. (2)

i	a_i	α_i	β_i	i	a_i	α_i	β_i
1	-1.8114918			8	1.9302835×10^{1}	-3	4
2	1.8596257	0	2	9	8.2997099	-1	5
3	-2.5992019	-1	2	10	-7.0732112	-2	6
4	3.8160201	-1	3	11	-1.2449543	-1	7
5	9.8899218	-2	3	12	5.9689394	-2	7
6	-9.0506900	-3	3	13	-1.8778413	-3	7
7	-2.4845810×10^{1}	-2	4	14	-4.1830091×10^{-1}	-1	8
P_c = 2886.3 kPa		T_c = 406.80 K		R_o = 8.31451 kJ/(kmol·K)			
ρ_c = 499 kg/m^3		M = 150.054 kg/kmol					

Cycle Performance Evaluation

For the purpose of discussing the applicability of HFE-245mc as a working fluid to the vapor-compression heat-pump systems, we have examined the theoretical cycle performance of high temperature heat-pump with new candidate, HFE-245mc. It is needless to mention that we do need a complete set of reliable information about essential thermodynamic properties of working fluid so as to evaluate the cycle performance. In case of HFE-245mc of the present interest, however, no literature values are available regarding the isobaric specific heat capacities in the ideal gas state, C_p^0, as a function of temperature and the heat of vaporization, Δh, which both are of essential importance to be incorporated with the present thermodynamic property formulations developed, eqs. (1) and (3).

According to the reason mentioned above, therefore, we have tried to apply the predictive methods to estimate these thermodynamic properties, i.e., $C_p^0(T)$ and $\Delta h(T)$, in the present analysis. Regarding the isobaric specific heat capacity, C_p^0, as a function of temperature, we have simply relied on the so-called group-contribution method in which some form of group-estimation method is involved based on the structure of molecule. For the present purpose we have used the method developed by Rihani and Doraiswamy [9] which is applicable to many types of organic compounds. The estimated correlation thus derived is given below as a function of temperature:

$$\frac{C_p^{\,0}}{R} = -0.5114 + 6.4291\times10^{-2}T - 4.7052\times10^{-5}T^2 + 1.6976\times10^{-8}T^3 \qquad (4)$$

where, C_p^0 in kJ/kg^{-1}·K^{-1} and T in K.

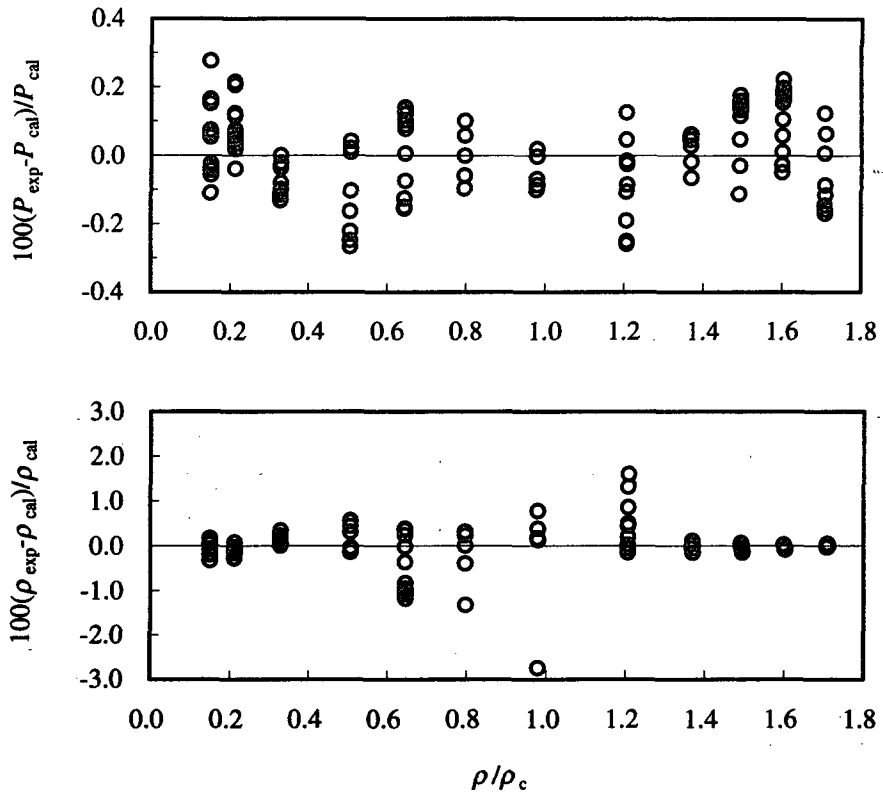


Figure 4. Pressure and density deviations of experimental *PVT* data from eq. (3)

Having applied the well-know thermodynamic relation to derive the specific enthalpy values from the present formulation, eq. (3), we can derive an expression for the specific enthalpy, $h(\rho,T)$, at specified density and temperature with an aid of the predicted $C_p^0(T)$ correlation, eq. (4). At this stage, we have simply applied eq. (3) to estimate the specific enthalpy values at different temperatures along the saturated vapor curve by a following procedure. Namely, by substituting eq. (1) into eq. (3) and applying the Newton-Raphson method, we can obtain the saturated vapor-density values at different temperatures and pressures. Then, by introducing thus-calculated saturated vapor-density values into the above-mentioned $h(\rho,T)$ equation, we can obtain the specific enthalpy values along the saturated vapor boundary.

On the other hand, we have applied the well-established Pitzer acentric-factor correlation [10] to predict the heat of vaporization at different temperatures. By combining these heat of vaporization values with the specific enthalpy values at the saturated vapor states, an important chart for refrigeration cycle, pressure-enthalpy diagram, has been prepared for HFE-245mc, for the first time, as shown in Fig. 5. Since the availability of experimental thermodynamic property measurements except the present study is still limited as discussed earlier, the *P-h* diagram given in Fig. 5 may still include some unpredicted uncertainties due to the applied predictive methods but we believe this chart is useful to discuss the engineering evaluation of cycle performance with HFE-245mc. It should be noted that the reference standards for the specific enthalpy and entropy values assigned here are 200.0 kJ/kg and 1.000 $kJ \cdot kg^{-1} \cdot K^{-1}$, respectively, at the saturated liquid condition at 273.15 K.

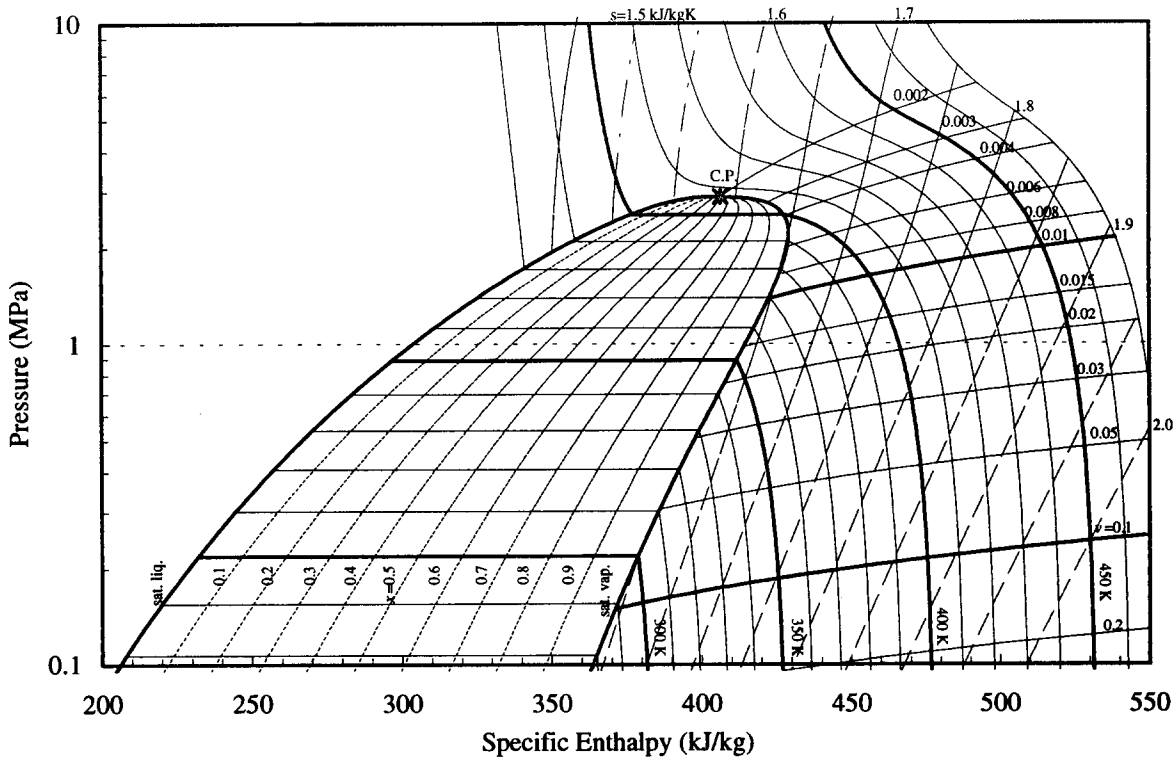


Figure 5. *P-h* diagram for HFE-245mc

It should also be noted that one of the most important and severe tests to examine the modeled formulation is feasible by computing the isobaric specific heat capacity behavior over an entire fluid phase. Figure 6 shows such a behavior along isobars which has been calculated from the present model, eq. (3), together with eq. (4). Again no measured C_p values are available for this compound to be compared with the present analytical results, it seems fair to mention that the thermodynamic behavior shown in Fig.6 is physically sound and reasonable.

Concerning the theoretical cycle performance evaluation of heat-pump systems with HFE-245mc, we have utilized the computed thermodynamic property values mentioned above together with the pressure-enthalpy diagram shown in Fig. 5. A series of comparison with R-114 which was used conventionally for high temperature heat-pump systems has been conducted at different operating conditions. Their results are summarized in Table 2, where we have assumed the superheat being 15 or 20 °C at the inlet of compressor but no subcool at the exit of condenser. Thermodynamic property values for R-114 are all calculated from the compilation [11].

It is recognized, from Table 2, that the heating effect by the heat-pumping cycle with HFE-245mc is always larger than that with R-114, whereas the COP_h values become lower by applying HFE-245mc instead of R-114. The gain in heating effect by applying HFE-245mc is 2-9 %, whereas the decrease in COP_h amounts 5-12 %, as far as the present comparisons with respect to the operating conditions given in Table 2 are concerned. It is also interesting to note that the reported COP_h value with HFE-245mc [1] at 100 °C in condensing temperature and at 50 °C in evaporating temperature with 15 °C in superheat was 5.01 that is slightly lower than

the present COP_h value, 5.20, as given in Table 2. It should be noted the cycle performance reported [1] was obtained exclusively based on the predicted thermodynamic properties of HFE-245mc and we believe the present results are more reliable than Ref. [1], since the present evaluation has been performed on the basis of experimental measurements and reliable formulations developed.

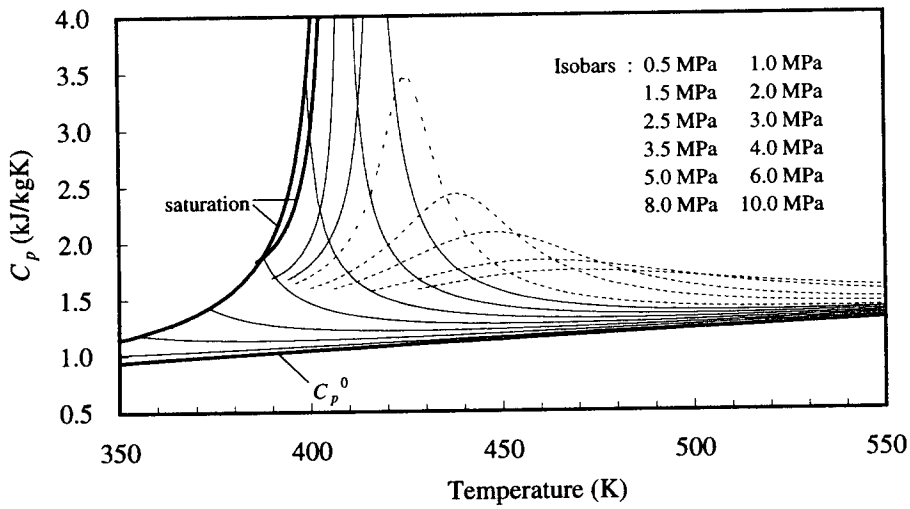


Figure 6. Isobaric specific heat capacities of HFE-245mc (densities up to 900 kg/m^3)

Table 2. Evaluated cycle performance (subcool = 0 °C)

			HFE-245mc		R-114	
Condensing Temperature (°C)	Evaporating Temperature (°C)	Superheat (°C)	Heating Effect (kJ/kg)	COP_h	Heating Effect (kJ/kg)	COP_h
100	40	20	100.8	4.19	92.1	4.43
100	50	15	98.3	5.20	90.1	5.48
100	60	15	101.4	6.90	92.5	7.21
105	40	20	94.6	3.71	87.5	3.94
105	50	15	92.1	4.53	85.4	4.79
105	60	15	95.2	5.89	87.0	6.37
110	40	20	88.1	3.28	82.5	3.52
110	50	15	85.5	3.94	80.4	4.22
110	60	15	88.6	5.05	82.9	5.35
115	40	20	81.0	2.88	77.1	3.14
115	50	20	84.1	3.55	79.5	3.84
115	60	15	81.6	4.33	77.5	4.67
120	40	20	73.4	2.50	71.5	2.79
120	50	20	76.5	3.07	73.9	3.38
120	60	15	74.0	3.68	71.9	4.06

Conclusion

In this study, an extensive set of vapor pressures and *PVT* properties of HFE-245mc has been measured. A vapor pressure correlation has been developed, and the critical pressure P_c = 2886.3 ±1.5 kPa which corresponds to the critical temperature T_c = 406.80 ±0.03 K has also been determined. The present experimental *PVT* measurements are the first set of data that cover the entire fluid phase and these measurements have been represented by the developed virial-expansion type equation of state. This equation of state is the first ever formulated based on the experimental data for HFE-245mc.

The derived thermodynamic properties have been calculated from the present model with an aid of the predicted C_p^0 and heat of vaporization values. A systematic comparison of the theoretical cycle performance have also been discussed in comparison with R-114. The results support the feasibility of using HFE-245mc to replace R-114 for high temperature heat-pump applications.

Acknowledgement

This research was partially supported by NEDO through RITE, and the authors are grateful to these organizations. We also wish to thank Akira Nakashima, a graduate student at Keio University, and Atsuko Uchimura, an undergraduate student at Keio University, for their assistance.

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Development of Hydrofluoroethers as Alternative Refrigerants and Other Applications

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Abstract

We have conducted a continuous search for new alternative refrigerants etc. At a previous conference, we showed that hydrofluoroethers have the ability to replace refrigerants. In this presentation, we will report further research results on refrigerants etc.
We will also present an interesting application of hydrofluoroethers in another field.

Fluorinated ethers have useful properties as candidates for CFC and HCFC alternatives. Among the fluorinated ethers, four compounds were selected as potential refrigerants, and thirteen compounds were selected as potential blowing agents.
We tested these ethers for practical use.

Research Organization

Under the commission of the New Energy and Industry Technology Development Organization(NEDO), the Research Institute of Innovative Technology for the Earth(RITE) conducted a joint research project with the National Institute of Materials and Chemical Research(NIMC) and National Institute for Resource and Environment(NIRE) by the researchers from ten private sectors.

Selected Fluorinated Ethers

The purpose of this research is to survey a new compound with a completely different molecular structure to that of CFCs and their alternatives, HCFCs and HFCs. Due to environmental issue, any new alternative must have the following properties:

1. Not contribute to ozone layer depletion
2. Break down in the atmosphere soon after its useful life has ended
3. Have little greenhouse effect
4. Have properties similar to those of CFCs and HCFCs
5. Be nonflammable
6. Have low toxicity

By measuring and estimation of characteristics, four fluorinated ethers as candidates for refrigerant alternatives and thirteen fluorinated ethers (shown in Table 7) as candidates for blowing agents were selected.
Some properties of alternative refrigerants in comparison with HFCs, HCFCs and CFCs are shown in Table 1.

Table 1. Some Properties of Fluorinated Ethers in Comparison with HFCs ,HCFCs and CFCs

Compound	Boiling Point [°C]	Critical Temp. [°C]	Critical Press. [Mpa]	Liquid Density [kg/m^3]	Specific Heat Ratio	Lifetime [y]	GWP [100y]	ODP
CFC-11	23.8	198.0	4.41	1414	1.126	50	4000	1.0
HCFC-123	27.7	183.7	3.67	1397		1.4	93	0.02
HFE-347mcc	34.2	164.5	2.48	1330		5.6	368	0
HFE-347mmy	29.5	160.8	2.55	1380	1.059	4.3	485	0
HFC-245fa	15.3	157.5	3.64	1291		8.4	820	0
CFC-114	3.8	145.6	3.26	1375	1.084	300	9300	1.0
HFE-245mc	6.0	133.7	2.89	1185	1.074	6.5	622	0
HFE-227me	-9.6	104.1	2.62	1262	1.063	>20		0
CFC-12	-29.8	111.8	4.13	1212	1.136	102	8500	0.9
HFC-134a	-26.5	101.5	4.06	1102		14.6	1300	0
HCFC-22	-40.8	92.2	4.99	1082	1.184	13	1700	0.055
R-410A	-51.6	71.5	4.92	909			1730	0
R-407C	-43.6	85.6	4.61	1014			1360	0

Chemical Formula:
CFC-11: CCl_3F; HCFC-123: $CHCl_2CF_3$; HFE-347mcc: $CF_3CF_2CF_2OCH_3$; HFE-347mmy: $(CF_3)_2CFOCH_3$; HFC-245fa: $CF_3CH_2CHF_2$;
CFC-114: $CClF_2CClF_2$; HFE-245mc: $CF_3CF_2OCH_3$; HFE-227me: $CF_3CHFOCF_3$;
CFC-12: CCl_2F_2; HFC-134a: CF_3CH_2F;
HCFC-22: $CHClF_2$; R-410A: R32/125 ; R407C: R32/125/134a

Characteristic Properties

Thermal Stability of Selected Fluorinated Ethers

We examines the possibility of using fluorinated ethers as refrigerants for heat recovery systems, as one of their applications.
Since most waste heat is produced at 30~60℃, fluorinated ethers used as refrigerants for industrial heat recovery systems must have a boiling point at an appropriate level to use waste heat and be stable at a high temperature range of between 60℃~150℃. Thermal stability tests were done at temperature of 150 and 175 ℃ for 30 days. HFE-245mc has a 5.6℃ boiling point and was stable under the experimental conditions as shown in Table 2.

Table 2. Thermal Stability of Selected Ether (HFE-245mc)

Heating Condition	Test Piece					
	Non	SUS-304	Fe(SS400)	Cu	Al	Lubricant
150℃ 30days	O	O	O	O	O	O
175℃ 30days	O	O	O	O	O	O

Sample in the sealed glass tube (10mm ϕ × 180mm)
Evaluation: O Stable , X Unstable
Property of lubricant oil was shown in Table 5

Electric Properties

Electric properties of refrigerants are the one of the important properties for hermetic compressor because the electric motor of the compressor is dipped into the refrigerants.

Volume electrical resistance and dielectric constant were measured and compared with HCFCs and HFCs. The results are shown in Table 3, and Table 4 respectively.
The value of the dielectric constant of HFE-245mc lay between that of HCFC-22 and

HFC-134a. Volume electrical resistance of HFE-245mc was also compared with HCFC-22, HFC-134a and CFC-113.

In conclusion, HFE-245mc had almost same electric properties as HCFC-22 and HFC-134a.

Table 3. Volume Electrical Resistance

Compound	Volume Electrical Resistance [Ω·m]	Temp. [°C]	Applied		
			Voltage [V]	Frequency [Hz]	Pressure [Mpa]
HFE-245mc	0.11×10^8	22	1	1000	
HFE-245mc	0.99×10^6	30	1	DC	1.47
HCFC-22	1.8×10^6	22	1	1000	
HCFC-22	5.1×10^6	30	1	DC	1.57
HFC-134a	2.5×10^6	22	1	1000	
HFC-134a	7.3×10^6	30	1	DC	1.57
CFC-113	3.3×10^9	30	1	DC	1.08

Table 4. Dielectric Constant

Compound	Dielectric Constant	Applied		
		Temp. [°C]	Frequency [Hz]	Pressure [Mpa]
HFE-245mc	7.2	30	100	1.57
HCFC-22	6.0	30	100	1.57
HFC-134a	9.0	30	100	1.57
CFC-113	2.4	30	100	1.08

Selection of Lubricant Oil

As the selected ethers dissolve slightly into the mineral oil, a lubricant suitable for a compression type cycle performance test unit has to be selected. A polyolester type oil was selected and tested. Some properties are shown in Table 5.

Table 5. Properties of Lubricant Oil and Critical Solubility Temperature

Properties of Lubricant Oil	
Density at 15 ℃	1010.8 Kg/m^3
Dynamic Viscosity at 40 ℃	62.4 mm^2/s
at 100 ℃	7.8 mm^2/s
Viscosity Index	89
Total Acidity	0.0 (mg KOH/g)
Water Content	96 ppm
Volume Electrical Resistance 〔Ωcm〕	2.7×10^{13}
Critical Solubility Temperature (CST) *	
Lower (LCST)	-5 ℃
Upper (UCST)	> 80 ℃

* Oil : HFE-245mc = 2 : 8 (wt ratio)

Performance Evaluation

The preliminary cycle performance evaluation of the fluorinated ethers was done using the apparatus shown in Figure 1 and compared with CFC-114 . HFE-245mc had almost same heating capacity as CFC-114.

Refrigerant characteristics are shown in Table 6 calculated by the prediction method (THEDYNA) developed by our project.

Another Application - Foam Blowing Agent

Vapor thermal conductivity is an important factor for foam blowing agents. We measured the thermal conductivity at vapor phase and found these fluorinated ethers

have low thermal conductivity and therefore these ethers will be candidates for foam blowing agents as shown in Table 7.

Figure 1 Cycle Performance Test Apparatus

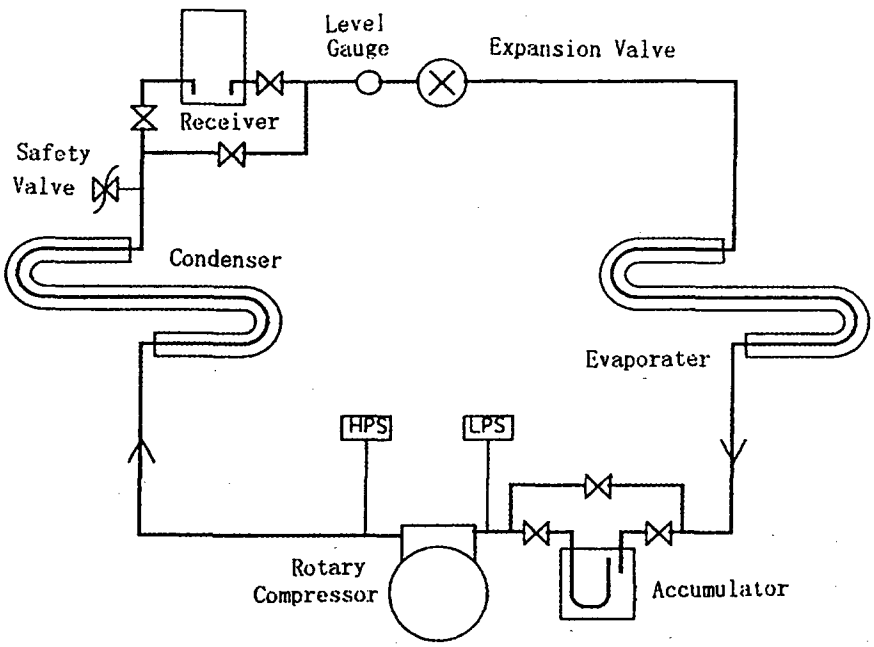

Table 6. Cycle Performance Evaluation

Compound	Heat Recovery Condition Te = 30 ℃ Tc = 80 ℃				COP(H)
	Superheat Temp. [℃]	Evaporation Pressure [Mpa]	Condence Pressure [Mpa]	Heating Capacity [kJ/m^3]	
CFC-11	25	0.127	0.523	1164	6.16
HCFC-123	25	0.111	0.476	1016	6.09
CFC-114	25	0.255	0.940	1873	5.67
HFE-245fa	25	0.173	0.750	1499	5.85
HFE-245mc	25	0.244	0.963	1806	5.49
HFE-347mcc	25	0.100	0.480	873	5.59
HFE-347mmy	25	0.104	0.479	887	5.62
HFE-227me	25	0.278	1.410	2170	4.95

Data were obtained through THEDYNA(Prediction Method) calculations.

Table 7 Vapor Thermal Conductivity

Compound	Boiling Point [℃]	Vapor Thermal Conductivity [m W/m · K(50℃)]
$CHF_2CF_2OCH_2CF_3$	56.2	12.37
$CF_3CF_2OCF_2CHF_2$	22.0	12.68
$(CF_3)_2CHOCH_3$	51.0	12.68
$CF_3CF_2CF_2OCH_3$	34.2	12.79
$CF_3CF_2CH_2OCHF_2$	45.9	12.93
$(CF_3)_2CFOCH_3$	29.4	13.01
$CH_2FCF_2OCHF_2$	43.1	13.08
$CHF_2CF_2OCH_3$	37.2	13.34
$CF_3CHFOCF_3$	-9.6	13.44
$(CF_3)_2CHOCHF_2$	42.1	13.46
CHF_2OCHF_2	5.2	13.66
$CF_3CH_2OCHF_2$	26.1	13.75
$CF_3CF_2OCH_3$	5.6	13.81
$CF_3CH_2CF_2H$ (HFC-245fa)	15.3	13.86

Acknowledgements

This work was partially done by the current national project of developing CFCs alternatives titled "Development of New Refrigerant, Blowing Agents and Cleaning Solvents for Effective Use of Energy". We thank to the members of the project to present this paper.

HFC-245fa, A Chiller Refrigerant

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Abstract:

An evaluation of potential low pressure chiller refrigerants yielded HFC-245fa as a promising candidate for this application.

We have extensively measured the basic properties needed for the evaluation of this fluid as a refrigerant and will describe those physical properties in this paper. These properties and performance in typical chiller cycles are presented along with corresponding values for other low pressure chiller refrigerants, R-123 and R-11, and medium pressure refrigerant HFC-134a. An evaluation of the refrigerant's flammability properties has shown it to be non-flammable.

HFC-245fa appears to be an excellent refrigerant for new centrifugal water chillers. It offers comparable efficiency to other low pressure refrigerants along with higher capacity.

Introduction:

The majority of centrifugal chillers in service utilize a low pressures design, and use CFC-11 or HCFC-123 as the refrigerant. Higher pressure chillers are available, such as those using HFC -134a, but the market place continues to see a need for the low pressure machines. While HCFC-123 is available till the year 2020 for new equipment under current US regulations, studies have underway to identify an HFC alternative. We had reported earlier on use of HFC-245ca as a drop in replacement for CFC-11[1]. N. Dean Smith et. al[2]. have reported on HFC-245fa as a possible refrigerant in this application. HFC-245fa has higher vapor pressure than CFC-11 or HCFC-123 or HFC-245ca. In the past it was a cause of concern. This is because with a vapor pressure exceeding 15 psig at 115°F, HFC-245fa machines would require ASME pressure vessel

code adherence, thus increasing cost. On the other hand the increase in vapor pressure (or capacity) over HCFC-123 implies that the use of HFC-245fa could allow chiller manufacturers to extend the range of their current product offering.

Flammability:

Historically there has been inconsistencies among flammability test methods. The various methods gave conflicting results on flammability of many refrigerants. More recently, with publication of Standard 2182 by Underwriters Laboratories and the proposed modification to ANSI/ASHRAE Standard 34, currently out for public review as Addendum 34p, the flammability standards have become more defined and in many ways much more stringent, consistent, and reliable. We have tested both HFC-245fa and HFC-245ca by the proposed ASHRAE method. The results showed that HFC-245fa is non-flammable but the tests for HFC-245ca showed limited flammability. We also submitted a sample of HFC-245fa to the Underwriters Laboratories, who also tested this refrigerant and classified it under UL2182 standard as "practically nonflammable". This flammability classification of HFC-245fa is identical to that of more common refrigerants such as HFC-134a, HCFC-123, and HCFC-22.

Thermodynamic properties and cycles:

A Martin-Hou equation of state has been derived for HFC-245fa based on recent experimental data. PVT properties and the ideal gas heat capacity have been estimated using standard techniques. A thermodynamic cycle model has been modified to incorporate the equation of state. The equation-of-state parameters have been given in the appendix.

Using this model, a preliminary evaluation of the performance of HFC-245fa in chiller applications was conducted. The capacity was determined for a single stage cycle with an evaporating temperature of 40°F, condensing temperature of 95°F, and a 80% isentropic efficiency compressor. Table 1 shows the results for CFC-11, HCFC-123, HFC-245fa, and HFC-134a for various levels of subcooling. Based on constant displacement, R-245fa has significantly higher capacity (30 to 35%) than R-11 and still higher (50-55%) than R-123. As expected, the higher pressure refrigerant HFC-134a has considerable higher capacity than all the lower pressure refrigerants.

As is typical when comparing high ideal gas heat capacity refrigerants with a lower heat capacity one, the COP (efficiency) of HFC-245fa is lower than that of CFC-11, but this difference can be minimized when effects of subcooling and multistage operation are introduced[3]. In the next two tables, we compare the thermodynamic efficiency (expressed as kW/ton) of CFC-11, HCFC-123, HFC-245fa, and HFC-134a in the same chiller cycle as described above.

Table 1. Influence of subcooling on cooling capacity (Btu/hr per CFM) and choice of refrigerant (single stage)

Subcooling °F	CFC-11	HCFC-123	HFC-245fa	HFC-134a
0	764	649	999	4113
5	776	661	1023	4224
10	787	673	1047	4334
15	797	685	1072	4442
20	810	697	1096	4550

Table 2. Influence of subcooling on Energy consumption (kW/Ton) and choice of refrigerant (single stage)

Subcooling °F	CFC-11	HCFC-123	HFC-245fa	HFC-134a
0	0.529	0.536	0.548	0.569
5	0.521	0.526	0.535	0.554
10	0.513	0.517	0.524	0.540
15	0.507	0.508	0.513	0.527
20	0.499	0.499	0.502	0.514

Table 3. Influence of stages on energy consumption (kW/ton) and choice of refrigerant (no subcooling)

Stages	CFC-11	HCFC-123	HFC-245fa	HFC-134a
1	0.529	0.535	0.548	0.569
2	0.511	0.513	0.518	0.534
3	0.506	0.506	0.509	0.524

The above tables are based solely on thermodynamic properties. It is known from a number of studies on comparative efficiencies of refrigerants that the heat transfer properties, and pressure drop losses are improved by higher vapor densities and a similar trend should be expected with the higher pressure refrigerant, HFC-245fa. Thus, we could expect that the small thermodynamic efficiency differences between HFC-245fa and CFC-11 or HCFC-123 may be offset by lower system irreversibilities resulting in system efficiencies comparable to CFC-11 or HCFC-123 and at the same time afford a higher capacity.

Environmental Properties:

It is important, specially these days, to determine the environmental properties of the refrigerant as well as those of the atmospheric degradation products of the refrigerant. This assessment includes a calculation for the greenhouse warming potential (GWP), and an identification of the compounds formed from HFC-245fa once it is released into the atmosphere.

The Ozone Depletion Potential (ODP) would be zero since this compound does not contain chlorine atoms.

The Green House Warming Potential (GWP) for this compound relative to CO2 on a 100 year time horizon is 790, and was calculated by AER Inc. using complex atmospheric models. Key input parameters were the IR cross-sections measured at the Central Research Laboratory of AlliedSignal and the OH abstraction rate constants measured by Orkin et.al. [4] at NIST.

Studies by Chen *et.al*[5] regarding the atmospheric degradation of HFC-245fa have shown that this molecule would be ultimately broken down to simple inorganic compounds, HF and carbon dioxide. No long-lived organic degradation products will be produced.

Conclusions:

HFC-245fa shows considerable promise as a refrigerant for low pressure centrifugal water chillers. Although the slightly higher condensing pressure would require changes to R-11 or R-123 heat exchanger design, the higher capacity could extend the range of this type of centrifugal chillers. This can be done without any significant decrease in the high energy efficiency associated with this class of refrigerants. Other design changes and lubrication requirements for conventional low pressure equipment and components would need to be determined by the chiller OEM.

Acknowledgment:

We thank Ms. Hang T. Pham and Mr. Kane D. Cook for carrying out the measurements of the thermodynamic properties and Mr. Robert G. Richard for the flammability tests. We also thank AlliedSignal for permission to publish this work.

References:

1. H. M. Hughes, "Non-Ozone Depleting Refrigerants for Centrifugal Chillers", Proceeding of the 1992 International CFC and Halon Alternatives Conference; pp 41.
2. N. Dean Smith et.al., "Evaluation of HFC-245fa", Proceedings of the 1994 International CFC and Halon Alternatives Conference; pp 894.
3. H. M. Hughes, Preprint "Contemporary Fluorocarbons" to be presented at "Refrigerants for 21st Century" conference, Oct 1997.
4. V. L. Orkin et.al. , "Atmospheric Lifetimes of HFC-143a and HFC-245fa" Journal of Physical Chemistry, Vol. 100, pp 8907 (1996)
5. J. Chen et.al., "Kinetics and Mechanistic Studies for Reactions of HFC-245fa Initiated by H-Atom Abstraction Using Atomic Chlorine", Journal of Physical Chemistry A, Vol. 101, pp 2648 (1997).

APPENDIX : Thermodynamic Data and M-H e.o.s. of HFC-245fa

Critical Temperature	309.2 F
Critical Pressure	643 psia
Critical Density	32.4 Lb./cu.ft.
Boiling Pt.	59.2 F

Vapor Pressure Correlation

$\ln(P) = A + B/T + C\,T + D\,T^2$ where P is in Psia and T is in Rankine and

A = 51.4247
B = -13,163.4864
C = -0.063363
D = 3.5319848 E-4

Liquid Density Correlation

$D = D_c + \sum_{i=1}^{4} Di(1-Tr)^{i/3}$ where D is in Lb./cu.ft; D_c is the critical density;

Tr is the reduced temperature and
D1 = 57.64247727

D2 = 32.07204042
D3 = -14.9636984
D4 = 12.43868002

Ideal Gas Heat Capacity Correlation

$C^0_p = C_1 + C_2 T + C_3 T^2$

where C^0_p is in BTU/lb./R ; T is in Rankine and
C_1 = 5.794307E-2
C_2 = 3.312206E-4
C_3 = -8.6927147E-7

Martin Hou e.o.s. Correlation

$$P = \frac{RT}{(v-b)} + \sum_{i=2}^{5} \frac{Ai + BiT + Ci\exp(-KTr)}{(v-b)i}$$

where P is in PSIA;

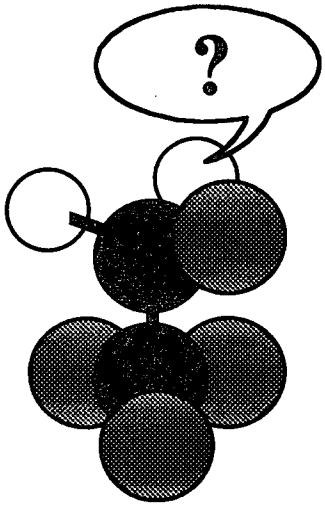
v is in cu.ft./lb.; T in Rankine and
Tr is the reduced temp.

R = 0.080056
b = 0.9762537322E-3
K = 5.475

I	Ai	Bi	Ci
2	-0.2952159398E1	0.9258840619E-3	-0.2841904479E2
3	0.9322916123E-1	-0.6595560768E-4	0.6675572224E0
4	-0.4368333351E-3	0	0
5	-0.1866620041E-5	0.4796018386E-8	-0.3022138088E-4

THREE IMPORTANT QUESTIONS TO ANSWER ON ALTERNATIVE REFRIGERANTS

By James R. Parsnow



The marketing hype continues on "alternative refrigerants". Driven by the Montreal Protocol and Federal laws like the U.S. Clean Air Act, the market potential for replacement or alternative refrigerants is an opportunity for an array of chemical companies to promote the "drop-in answer to your refrigerant needs". Unfortunately the public is being tasked with finding the right answer to their particular needs, and they are becoming increasingly confused by the advertisements and misleading promotions.

If the general public were well versed in chemistry, perhaps the alternative refrigerant choices would be easier to sort. However, most of the people who are faced with these choices are not chemists, but auto mechanics, service technicians, facility managers, property managers, engineers and numerous other professions who are addressing a mechanical device that uses refrigerants. Even environmentalists have been misled by the alternative refrigerant choices.

The following three questions should be considered to properly determine the best application of alternative refrigerants. They will help to sort the hype from good information.

1. Has the refrigerant been approved under the Environment Protection Agency (EPA), Significant New Alternatives Policy (SNAP)?

The EPA evaluates, approves, limits, or disapproves all alternative refrigerants in U.S. Applications. This evaluation includes the refrigerants ozone depleting potential, global warming potential, flammability and toxicity along with application limits. The SNAP program does not however approve or disapprove the performance or compatibility in a refrigeration system. Approval under the SNAP program is critical as those alternatives found unacceptable or violation of conditions or use of listed refrigerants is a violation of the U.S. Clean Air Act and may be subject to a $25,000 (U.S.) fine and up to five years in jail.

Produces of alternative refrigerants must submit information to the EPA SNAP program 90 days prior to marketing the product. After 90 days, if EPA has not had the opportunity to review the refrigerant, it may be sold and used. However, if after EPA review, the refrigerant is not approved for use or limited in application, owners may be stuck with an inventory or application that cannot be used legally. Under the Clean Air Act SNAP program, sale of any refrigerant is not restricted, however use can be legally restricted.

The SNAP program can be accessed on the internet under the address: **www.epa.gov/ozone/title6/snap/snap/snapfact.html.**

EPA administers the Clean Air Act by using industry standards for the recovery, recycling and reclamation of refrigerants. These standards are based on such organizations as the Society of Automotive Engineers (SAE), the Air-Conditioning and Refrigeration Institute (ARI) and the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE).

2. *Has the refrigerant been recognized by industry standards?*

Most advertisements on the "drop-in refrigerants" use trade names and designations along with promotional information that does not include the makeup of the refrigerant especially in the case of blended refrigerants. EPA along with the industry rely on the standards set forth by such organizations as SAE, ARI and ASHRAE to classify refrigerants for use. Not only do these standards provide limits on recovery, recycling and reclamation, but also on flammability and toxicity, along with proper application. See fig. #1 for reference.

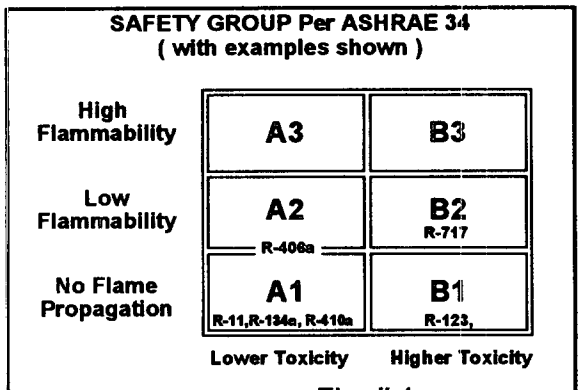


Fig. # 1

Standard ASHRAE 34, Number Designation and Safety Classification of Refrigerants provides a uniform rating of refrigerants for toxicity and flammability and also assigns refrigerant numbers (e.g. R-11, R-12, R-22, R-134a). Standard ASHRAE 15, Safety Code For Mechanical Refrigeration Rooms establishes safe practices in designing and installing equipment.

These standards provide factual data to sort out the marketing hype. Under ASHRAE 34, refrigerants assigned a number will also be listed as to flammability and toxicity. Flammability is tested according to the American Society of Testing Materials (ASTM) E-681 and the refrigerant is assigned to one of three categories: 1 - no flame propagation; 2 - low flammability or 3 - high flammability. For example, under ASHRAE 34, HFC-134a is classified in group 1, no flame propagation, because it is not flammable at any concentration in air at atmospheric pressure. On the other hand alternative refrigerants referred to as hydrocarbons ignite at concentrations as low as 2% by volume and are assigned to group 3. There are also two classifications for toxicity, "A" or "B". The "A" designates lower toxicity and the "B" higher toxicity. These designations are applied with the numbers (e.g. A1, B1) to provide the complete safety classification as noted in fig. #1. For example: CFC-11, 12 and HFC-134a are classified A1, no flame propagation, lower toxicity, HCFC-123 is assigned B1, no flame propagation, higher toxicity.

Blended refrigerants are assigned dual classifications, the first represents the safety classification for the refrigerant blend as it is purchased while the second represents the worst case that could be encountered if the components should separate during operation or during a leak. For example, R-410a (HFC32/125, 50%/50%) has been assigned a A1/A1, designation - no flame propagation, lower toxicity. Those blended refrigerants that

contain hydrocarbons or other flammable components may have two different ratings depending on the potential for flammability during applications. For example: R-406a HCFC-22/isobutane 600a/HCFC-142b, 55%/4%/41% is classified as a A1/A2, non-flammable as originally formulated, but could become flammable in application, such as a leak. Under ASHRAE Standard 15, this refrigerant would have to be applied per the worst condition A2. As a result under ASHRAE 15 Safety Code, R-406a would not be allowed for comfort cooling applications.

The assignment of an ASHRAE refrigerant designation has other benefits in that the number serves as a generic reference to the refrigerant rather than a manufacturers trade name. For example, R-134a is sold by Dupont under the brand name SUVA MP. Allied Signal refers to R-134a as Genetron 134a. In both cases, R-134a is the same.

Other industrial standards produced by the Air-Conditioning and Refrigeration Institute (ARI) provide guidance and in some cases are adopted by law. For example, ARI 700-93 is Specifications For Fluorocarbon and Other Refrigerants. Reclaimed refrigerants both in motor vehicles and stationary/commercial sectors must meet the requirements of ARI Standard 700 under the Clean Air Act Section 608. ARI Standard 700 specifies acceptable levels of refrigerant purity for fluorocarbon refrigerants. EPA is also considering an update to the Clean Air Act to incorporate another industry publication: Industry Recycling Guide (IRG-2). IRG-2 still refers to ARI 700 as the purity level standard.

Two other standards that should be reviewed are ASHRAE Guideline "K" Containers For Recovered Fluorocarbon Refrigerants and Guideline "N", Assignment Of Refrigerant Container Colors. All refrigerants are assigned a container color so that when in stock they can easily be distinguished from other type. For example, HFC-134a in cylinders is designated by light blue(sky). Guideline K is important as it references the proper markings that should be labeled on all refrigerant containers along with reference to Department of Transportation requirements for refrigerant containers.

3. *Has the original equipment manufacturer approved the new refrigerant for use in that particular application?*

Technically there are no "drop-in" refrigerants. Some come close, but there is always a compromise.

People considering the use of an alternative refrigerant should always consult with the original equipment manufacturer. As refrigerant is the blood of the equipment, the analogy applies; if a person's blood type was changed during a transfusion, the patient could die.

Material compatibility, compressor displacement, pressure, flow control, heat exchanger type and other application considerations must be thoroughly reviewed and tested. Results of not having an approved refrigerant application can result in problems from voided warranties to critical demise of the equipment.

For example, Refrigerant R-410a (Azeotrope of HFC-32 & 125, produced by Allied Signal, AZ20) is an excellent replacement for HCFC-22. The key word being "replacement".

However, this refrigerant is not a drop-in for all HCFC-22 existing equipment. One reason is pressure. For example, at 100° F (327.8c), HCFC-22 is at 210.7 psig(95.6 Kg) R-410a at 100° F (37.8c) is at 320.5 psig. (145.4 Kg). 34% higher pressure than HCFC-22.

Consult your original equipment manufacture for alternative refrigerant application!

Three critical questions that should be applied to any alternative refrigerant. The answers will sort through the advertising hype and provide factual data.

"There are no drop-in refrigerants, only alternatives"

ESSENTIAL REFERENCES

Guideline Standards

ASHRAE 34-1992:	Number designation and safety classification of refrigerants
ASHRAE 15-1994:	Safety code for mechanical refrigeration
ARI 740-93:	Performance of refrigerant recovery, recycling, and/or reclaiming equipment
ARI 700-93:	Specifications for fluorocarbon refrigerants
ASHRAE Guideline "K":	Containers for recovered fluorocarbon refrigerants
ASHRAE Guideline "N":	Assignment of refrigerant container colors
U.S. EPA Guidelines & Law:	Clean Air Act;, final ruling of Section 608 of CAA; dated May 14, 1993; EPA Section 114 Letter; EPA Action Guidelines

Air Conditioning and Refrigeration Institute (ARI)
4301 North Fairfax Drive, Suite 425, Arlington, VA 22203
Phone: (703) 524-8800 Fax: (703) 528-3816

American Society of Heating, Refrigerating and Air Conditioning Engineers, Inc. (ASHRAE)
1791 Tullie Circle, NE, Atlanta, GA 30329
Phone: (404) 636-8400 Fax: (404) 321-5478

U.S. Environmental Protection Agency (U.S. EPA)
401 M. Street, SW, Washington, DC 20460
EPA Hotline: 1-800-296-1996

ASHRAE Number Assignments For Refrigerant Blends And Compounds

(*Pending approval at time of article publication)

ASHRAE 34 Number	Manufacturer's Name	Components	Composition Weight %	Safety Group*	Replaces Refrigerant	Container Color	Class** Number
22	Allied Signal, Dupont, Others	True Compound	CHF2CL	A1	--	Light Green	11
123	Dupont	True Compound	C2HF3CL2	B2	--	Light Blue-Gray	1
134a	Dupont, Allied Signal, ICI, Others	True Compound	C2H2F4	A1	--	Light Blue	11
401A	Dupont MP 39	R-22 R-152a R-124	53/13/3	A1/A1	R-12	Light Purple	11
401B	Dupont MP66	R-22 R-152a R-124	61/11/28	A1/A1	R-12	Yellow-Brown	11
401C	Dupont MP52	R-22 R-152a R-124	33/15/52	A1/A1	R-12	Blue-Green	11
402A	Dupont HP80	R-125 R-290 R-22	60/2/38	A1/A1	R-502	Light Brown	111
402B	Dupont HP81	R-125 R-290 R-22	38/2/60	A1/A1	R-502	Green-Brown	111
403A	Rone-Poulenc 69S	R-290 R-22 R-218	5/75/20	A1/A1	R-502	--	--
403B	Rone-Poulenc 69L	R-290 R-22 R-218	5/56/39	A1/A1			
404A	Dupont HP62	R-125 R-143a R-134a	44/52/4	A1/A1	R-502	Orange	111
405A	Greencool G2015	R-22 R-152a R-142b R-C318	45/7/5.5/42.5	A1/A1	R-12	--	--
406A	Monroe Air Tech GHG-12	R-22 R-600a R-142b	55/4/41	A1/A2	R-12	--	--
407A	ICI Klea 60	R-32 R-125 R-134a	20/40/40	A1/A1	R-22	Lime-Green	111
407B	ICI Klea 61	R-32 R-125 R-134a	10/70/20	A1/A1	R-22	Cream	111

407C	Dupont AC9000/ICI Klea 66	R-32 R-125 R-134a	23/25/52	A1/A1	R-22	Medium-Brown	111
407D	ICI Klea	R-32 R-125 R-134a	15/15/70	A1/A1			
408A	Atochem FX 10	R-125 R-143a R-22	7/46/47	A1/A1	R-502	Medium-Purple	111
409A	Atochem FX 56	R-22 R-124 R-142b	60/25/15	A1/A1	R-12	Medium-Brown	11
409B	Atochem FX 57	R-22 R-124 R-142b	65/25/10	A1/A1			
410A	Allied Signal AZ20	R-32 R-125	50/50	A1/A1			
410B	Dupont AC 9100	R-32 R-125	45/55	A1/A1	R-22	Maroon	111
411A	Greencool G2018A	R-1270 R-22 R-152a	1.5/87.5/11	A1/A2	R-22	--	--
411B	Greencool G2018B	R-1270 R-22 R-152a	3/94/3	A1/A2	R-502	--	--
412A	ICI Arcton TP5R	R-22 R-218 R-142b	70/5/25	A1/A2	--	--	--
*413A	Rhone-Poulenc Isceon 49	R-218 R-134a R-600a	9/88/3	A1/A2	--	--	--
*414A	Peoples Welding Supply GHG-X4	R-22 R-124 R-600a R-142b	51.0/28.5/4.0 /16.5	A1/A1			
*414B	ICOR International Inc.HOT SHOT	R-22 R-124 R-600a R-142b	50.0/39/1.5/ 9.5	A1/A1			
507	Allied Signal AZ50	R-125 R-143a	50/50	A1	R502/22	Blue-Green	111
508	ICI Klea 5R3	R-23 R-116	39/61	A1	R-503	--	--
509	ICI Arcton TP5R2	R-22 R-218	44/56	A1	--	--	--

*Safety Group per ASHRAE-34
A1 = Low toxicity, Non-flammable
A2 = Low toxicity, Flammable
B2 = Higher toxicity, Non flammable
B2 = Higher toxicity, Non flammable

**Class 1: boiling point .68F. Packaged in drums
Class II: low pressure Title 49 CRF, Normally in cylinders <260 psig
Class III: high pressure, compressed gas per Title 49 CFR min. press. cylinder <260 psig
Class IV: flammable refrigerants

EVALUATION OF REFRIGERANT OIL AND SLIDING MATERIALS FOR ALTERNATIVE REFRIGERANT

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Yukio Fudemato, Hideki Matsuura, Masaki Nomura
Daikin Industries Ltd

ABSTRUCT

The most difficult problem of the reliability of compressors is the selection and evaluation of refrigerant oils and sliding materials for application of HFC refrigerants. The primary selection of refrigerant oils would be carried out based on their viscosity, the viscosity characteristics under high pressure should be taken into consideration since there exists some mixed lubrication depending on conditions. Therefore, pressure viscosity coefficient was measured by utilizing the optical interference method. The measured values of HS-POE (polyol ester) and PVE (polyvinyl ether) were correlated with oil film sustaining ability evaluated by electric resistivity method. These measurements showed the good result of PVE.

As for the sliding materials, the evaluation of several materials for journal bearing and oldham ring, which components revealed some problems in durability tests of the scroll compressor, were conducted with using the bearing testing machine and frictional wear testing equipment in the refrigerant enveronment. Test results led to pick up the most suitable materials.

INTODUCTION

It has been widely reported that the extreme pressure effect can be severely reduced because of the lack of chlorine in HFC refrigerants since the application of these refrigerants was examined. The most remarkable examples are shown in Figure 1 and 2. Figure 1[1)] reveals seizure load of the shell four ball test under circumstances of different types of refrigerants. This result clearly shows the difference of the seizure loads of CFC, HCFC and HFC, and also the more chlorine refrigerants contains, the higher seizure load they have. Figure 2 shows the changing of seizure load measured by four ball seizing test in the case that the concentration of refrigerant in refrigerant oil was increased. It can be clearly seen that the difference of refrigerant oil types was negligible up to certain concentrations, and over this point, the anti-seizing effect of chlorine became apparent. Therefore, the durability test of the scroll compressor as shown in Figure 3 was carried out. After the test, wears were

observed on the sliding surface of the journal bearing and oldham ring. This result would be due not only to the extreme pressure effect of refrigerants but also to the lubricity of refrigerant oils.

In this study, lubricity of HFC refrigeration oils and materials of sliding components were investigated.

EVALUATION

1. Selection of refrigeration oils

The required basic characteristics for refrigerant oils are miscibility with refrigerants, stability (against heat, acid, water and refrigerant), lubricity, electrical insulation and pour point of fluidity at low temperature. As for lubricity, the effect of fluid film lubrication would be primarily taken into account, (i.e., the selection of refrigerant oil is based on viscosity) since viscosity of oil is strongly related to oil film formation, frictional wear loss, sealing and cooling. Also viscosity change by temperature and pressure is the important factors, and types of oils and additives come next.

Here the above mentioned characteristics of the following materials are listed in Table 1[2),3),4)], HS-POE which has been mainly studied as HFC refrigerant lubricant, PVE which has been currently paid attention to and mineral oil which has been most widely used. The concerned problems from this table is stability of POE (i.e., hydrolysis) and viscosity for lubrication. As for stability, extensive studies have been conducted by many researchers including the authors, please refer to somewhere else.

Against this background, the oil film sustaining ability of lubricant oil, which is directly related to lubricity, especially to frictional wear, was investigated in this study. The oil film sustaining ability has often been evaluated by viscosity only, however, roller bearing, vane tip of rotary compressor, inclination of journal bearing experiences extremely high pressure, resulting in elastic deformation. On such sliding parts, the viscosity of lubrication oil exponentially increases due to the extremely high pressure and the EHL (elastohydrodynamic lubrication) oil film is formed. Therefore, viscosity characteristics under high pressure needs to be investigated. Accordingly EHL oil film thickness was measured by most commonly used optical interferometer. The oil film formation ability of refrigerant oils at 40 ℃ was shown in Table 2. Here coefficient of EHL oil film thickness is the product of pressure viscosity coefficient and initial viscosity given by the following equation;

$$K_{EHL} \text{ (coefficient of oil film thickness)} = \eta^{0.67} \cdot \alpha^{0.53}$$

Since refrigerant is normally dissolved into refrigerant oil on the compressor operation,

oil film thickness of refrigerant and refrigeration lubricant mixtures was measured under the same load and the calculated pressure viscosity coefficient was shown as a function of viscosity (i.e., different mixing ratio of refrigerant and refrigeration oil) in the Figure 4. Although compressors are operated in a wide variety of conditions, the comparison of refrigerant oils at a certain condition (ambient pressure and temperature in the shell bottom: 5 kg/cm^2 and 70℃, respectively) can be as follows; the viscosity of R22 and conventionally used mineral oil (VG56) mixture is 9.0 cP and that of R407C and PVE is 11.3 cP. In this case, coefficients of EHL oil film thickness of these mixtures are approximately 2.7, which means that they have basically the same oil film formation ability. Although POE show the close result, the ability is somewhat lower since its pressure viscosity coefficient is smaller compared to PVE.

Next, oil film breakage loads of refrigerant oils were measured under the refrigerant circumstance by utilizing the four ball test equipment and results were revealed in Figure 5[2]. In this figure, the ordinate and the abscissa show the insulating ratio in percentage and the load, respectively. From this result, it can be easily seen that metal contact took place completely at loading force of 470N for POE and of 950N for PVE, confirming that PVE has more ability of oil film formation.

In case that lubrication condition becomes severe such as mixed lubrication or boundary lubrication, the oil film is broken down thermally or mechanically to increase remarkably the friction and wear, resulting in seize. In order to reduce the frictional wear under such conditions, oiliness agent and extreme pressure agent are often applied to. There are many kinds of additives to obtain this effect such as sulfide, chloride and phosphide, and relatively stable phosphoric ester is most commonly used as lubricant for compressors.

There are some studies of the effect of these additives. Hirano et al.[5] and Muraki et al.[6] reported the additive effects of phosphate ester into POE and the mechanism of wear. Their finding is that the optimal amount of phosphate ester is 1 to 3 %, which gives sufficient additive effects. However, as additive is consumed, frictional wear rapidly increases. Also since POE are resolved by heat on a sliding surface, it is difficult not to generate metallic soap, which may result in the capillary tube clogging.

On the other hand, Kim et al.[7] studied the additive effect of phosphate ester in PVE. They reported that the reduction in coefficient of friction was not observed, but the amount of wear was reduced.

From above mentioned evaluations, it can be concluded that VG68 PVE has the almost same oil film formation ability as VG56 mineral oil does. Also the

conventionally used tricresyl phosphate are effective to compensate for the loss of anti-seizing effect of non-chlorinated refrigerants. However, great care have to be taken of for the selection of agents, since highly reactive agents generate sludge and clog a capillary tube.

With considering the oil film formation ability and the additive effect of extreme pressure agents, PVE is the most desirable refrigeration oil for HFC refrigerants.

Up to here, the refrigerant oil was evaluated based on viscosity to sustain the oil film, the lubrication condition in a compressor is, however, complex mixed one of solid, boundary and fluid film lubrication. Accordingly it is difficult to evaluate the lubrication only by oil. Thus, the evaluation of frictional characteristics of sliding components is needed.

2. The Selection of Journal Bearing Material for Scroll Compressor

The major difference between the mineral oil and POE and PVE in durability tests was observed in ON-OFF operation, especially when refrigerant oils were diluted much by refrigerant . This would coincide with the results of the previous section. Contrary to it, oil film was sufficient and major frictional wear was not observed in the case of the less diluted operation condition. Therefore, seizing tests as a function of refrigerant concentration and wear tests for relatively high refrigerant concentration were conducted in the refrigerant atmosphere. Test materials were two types of aluminum alloys, lead bronze and dry bearing (resin over porously sintered bronze particles), and the material of the driving shaft was cast iron as shown in Table 3. The combinations of refrigerant and refrigeration oils were R22/mineral oil and R407C/PVE. The overview of the test equipment is shown in Figure 6 and the results are summarized in Figure 7 to 9.

First, Figure 7 shows ratio of seizure load (ordinate) for different kinds of materials(abscissa). It can be seen from this figure that R407C has smaller seizure loads, compared to R22, for all materials. Also the higher the refrigerant concentration is, the larger the seizure load becomes. This would be due to the effects of the extreme pressure and cooling by refrigerant described in earlier section. Moreover, the hardness of metals tends to reduce the seizure load.

Next, ratio of seizure pressure was plotted in Figure 8 for different materials. It can be seen that R22/lead bronze showed apparently different tendency as the other combinations. Although the reason of this is open, the result is correlated with the

compressor test result to some degree. In the tests of the refrigerant only, the material resistive to dry friction showed a good result not like to be seen in the seizure load test.

Finally wear amounts for the same materials of above were revealed in Figure 9. Though the tests were conducted at the fairly high refrigerant concentrations, higher hardness metals had good result as well as the result in Figure 8.

The result of the journal bearing test discussed in this section is correlated to one of the durability tests of compressors. Therefore, the dry bearing which consists of two lamella of resin and porously sintered bronze particles was selected as the material for the HFC compressor journal bearing, with considering of these results and the circumstances of sliding parts, and common use for R22. In the case of HFC use only, lead bronze bearing can be applied.

3. Selection of Material for Oldham Ring

Being different from journal bearing, the wear problem of oldham ring has come rise to in the transition of R22 to HFC. Since refrigerant concentration is not high, the oil film formation ability can not simply explain this phenomenon.

It is a well known fact that increase in silicon content generally improves anti-wear of aluminum alloy[8]. Thus, wear tests of five different silicon contents (i.e., different hardness) of aluminum alloys including the currently used material were conducted. The test materials are listed in Table 4. Silicon contents of candidate materials are about 10 % to 20 %, and Rockwell Hardness HRB of them are 35 to 85. An overview of the test equipment is shown in Figure 10, which test is generally called pin on disk test. The combinations of refrigerant and refrigeration oil are R22 with mineral oil and R407C with PVE. The result was shown in Figure 11, where the ratio of wear amount in ordinate was plotted as a function of average contact pressure in abscissa.

As for the currently used material, the wear amount difference between R22/mineral oil and R407C/PVE was noticeably observed, which met agreement with the result from tests in compressors. Then, the comparison of wear amounts of materials of higher silicon content with R407C/PVE turned out that suppressing the wear amount as low as that of R22/mineral oil was possible. It would generally true that silicon content largely influences on anti-wear, diameter of primary Si crystal is not apparently correlated to wear and matrix hardness is somewhat related to. Therefore, suppressing wear of oldham ring is possible by selecting an hyper-eutectic Si-Al crystal material and controlling its diameter (since primary Si crystal can put bad influences on wear of other sliding parts and processability).

CONCLUSION

In order to improve the reliability of lubrication for HFC scroll compressor;

1) As lubrication oil, viscosity grade VG 68 PVE, which is superior in oil film forming ability, was selected.

Also as the materials revealed shortcomings in durability tests;

2) For journal bearing material of compressor, dry bearing (resin over porously sintered bronze particles) or lead bronze was selected with consideration of environment and lubrication conditions and inclination of the bearing.
3) For the oldham ring material, anti-wearing hyper-eutectic Si-Al crystal was selected and the dimension was optimized.

The selections and changings mentioned above enabled the development of highly reliable scroll compresor.

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Table-1. Characteristics of candidate refrigerant oils

	mineral oil	HS-POE	PVE
miscibility U-CST[℃] R407C/R410A	10 (R22)	-15/10	-50> /-45
stability	—	poor in hydrolysis	≒mineral oil
elect. resistivity	10E14	10E13	10E13～10E14
pour point	-35	-40	-37.5
viscosity	56	68	68
viscosity index	16	88	79

Table-2. EHL oil film sustaining ability of refrigerant oils@40℃

refrigerant oil	viscosity [cP]	pressure viscosity coefficient [1/GPa]	coefficient of EHL oil film thickness
suniso4GS	51.1	24.3	12.5
HS-POE	63.6	16.7	11.9
PVE	60.1	21.3	13.0

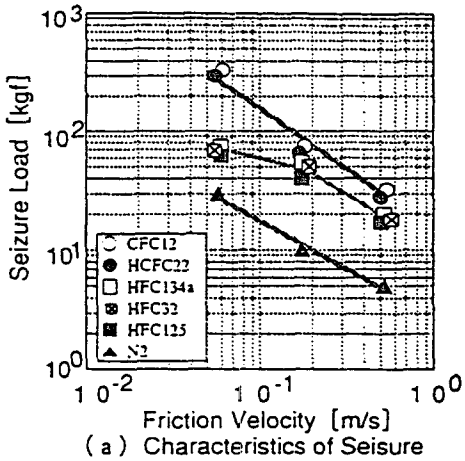
Table-3. Candidate materials for journal bearing

material		chemical component	hardness Hv
A	aluminum alloy	Al-Cu-Sn-Pb-Sb-Si	42
B		Al-Cu-Sn-Pb-Si	48
C	lead bronze	Cu-Sn-Pb-C	50
D	dry bearing	Cu-Sn (bronze lamella) PTFE-Pb(resin lamella)	80 —

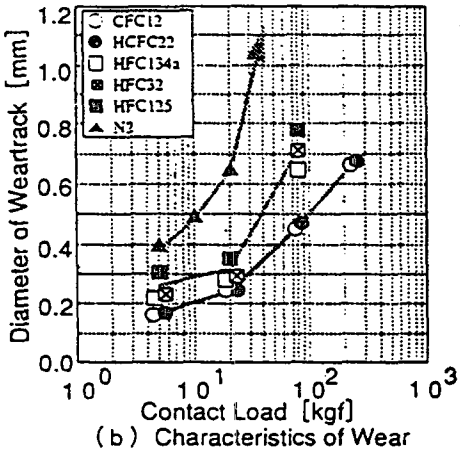
Table-4. Candidate materials for oldham ring

material	chemical component	Si particle size [μm]	
①	Al-Si-Fe-Cu-Mn-Mg-Zn-Ni-Sn	hypoeutectic	
②	Al-Si-Fe-Cu-Mn-Mg-Zn-Ni-Ti-P	hypereutectoid	40～95
③	Al-Si-Fe-Cu-Mn-Mg-Zn-Ni-Sn-P		20～40
④			
⑤	Al-Si-Fe-Cu-Mn-Mg-Zn-Ti-Cr		30～50

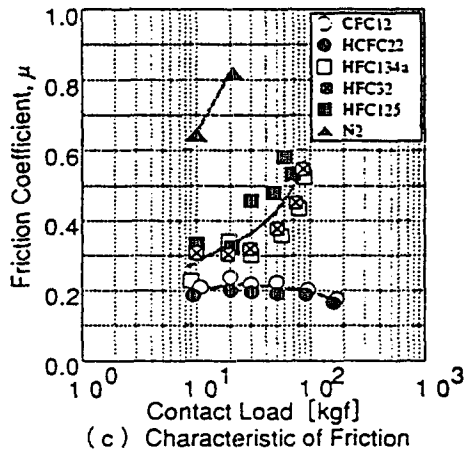
		①	②	③	④	⑤
silicon content (%)		9.6～12	16～18	13.5～15.5	16～18	16～17
hardness	HRB	34～35	67～70	60～70	62～74	(79～83)
	Hv	80～100	—	124～130	137～143	(149～158)
	HB	75～	(94～123)			130～138



(a) Characteristics of Seisure

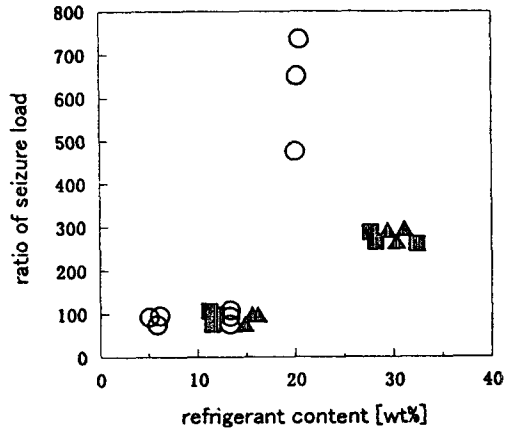


(b) Characteristics of Wear



(c) Characteristic of Friction

Fig.-1 Characteristics of fricion and in dry furon gas
(printed from (1))



O:R22/mineral oil ▲:R407C/HS-POE
▩:R407C/PVE

ratio of seizure load =
(tested seizure load/seizure load under R22+ mineral oil at 5% refrigerant content)*100

Fig.-2 Result of seizing test by four ball

test conditions rotation frequency : 2000r.p.m.
temperature : room temp.

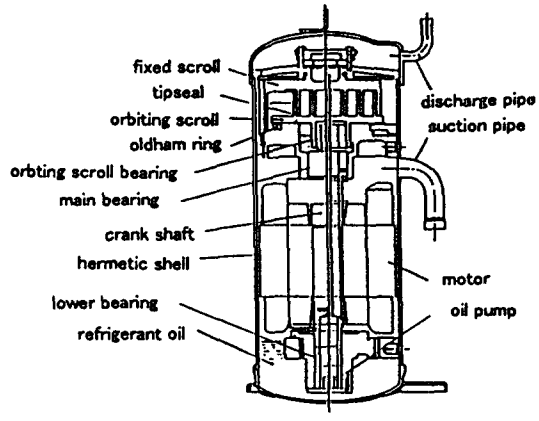


Fig.-3 scroll compressor

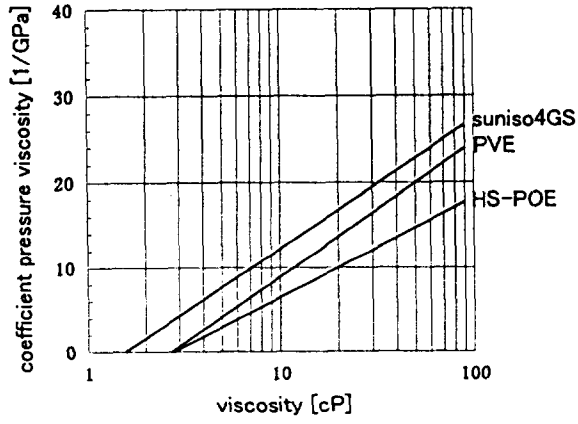


Fig.-4 Characteristics of high pressure viscosity

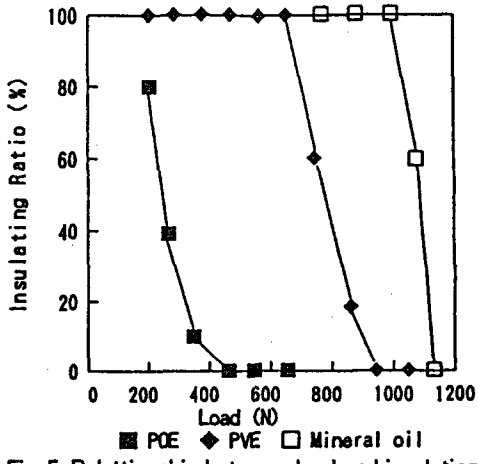
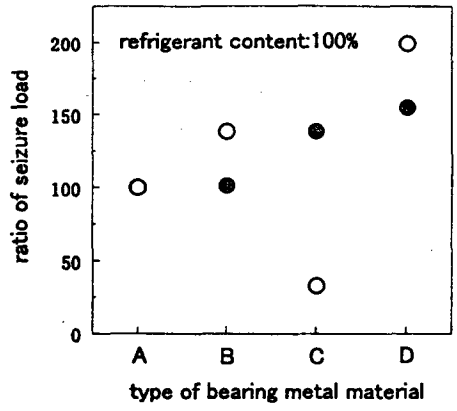


Fig-5. Relattionship between load and insulating ratio of frictional surfaces
(printed from (2))



ratio of seizure load =
(testing seizure load / seizure load under R22 + M.O. with A material) *100

Fig.-8 Results of seizing test

test conditions ON/OFF operation
temp. : room temp.

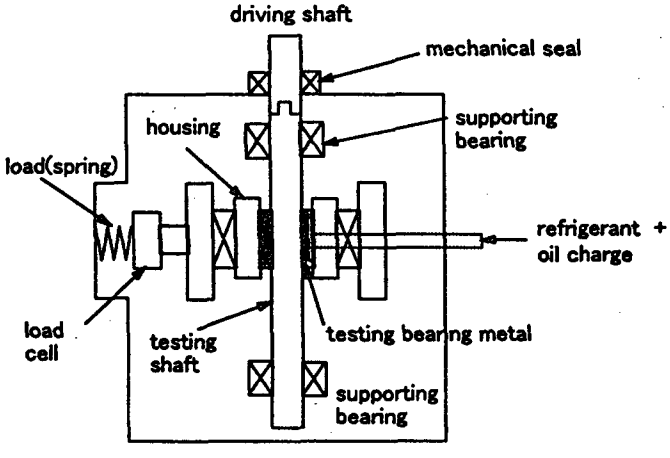


Fig.-6 Bearing testing machine under circumstances of refrigerant

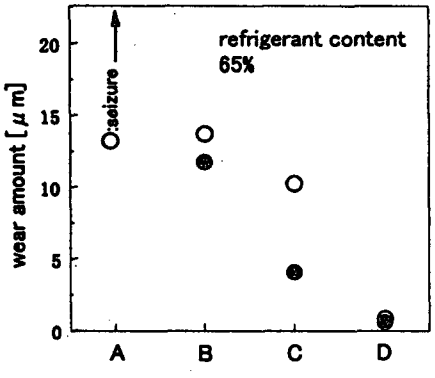
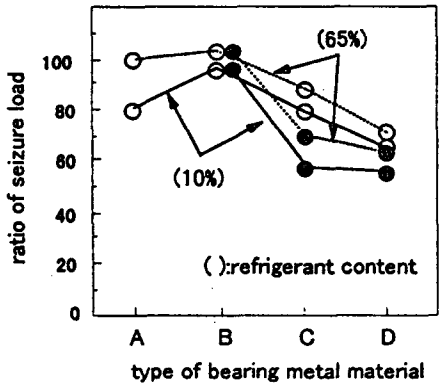


Fig.-9 Results of wear test

test conditions ON/OFF operation
temp. : room temp..
load : 60kgf/cm2



ratio of seizure load =
(testing seizure load/seizure load under R22+M.O. with A material)*100

Fig.-7 Results of seizing test

test conditions rotation frequency : 3600r.p.m.
temperature : room temp~

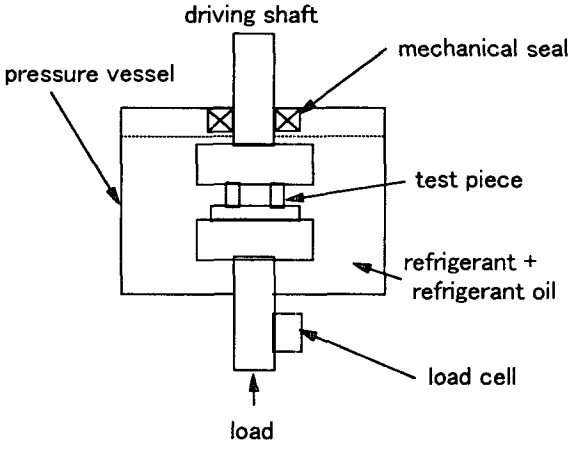
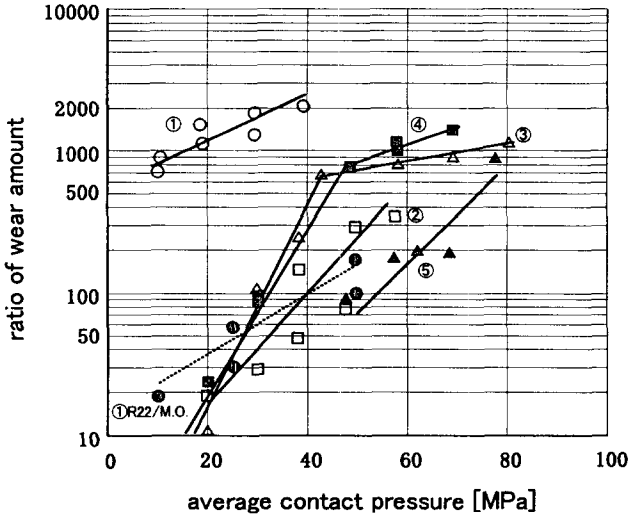


Fig.-10 Friction wear testing equippment under circumstances of refrigerant



ratio of wea amount =
(testing wear amount/wear amount under R22+M.O. at 40MPa) * 100

Fig.-11 Results of wear test for oldham ring materials

test conditons sliding velosity:2m/sec
sliding length:7.2km
ambient temperature:100℃
refrigerant content:12%

HFC-134a Qualification
Industry Refrigerator Capillary Data

Richard DeVos, Frigidaire Company Refrigerator Division
and
Thomas H. Davis, Ph.D., General Electric Appliances - Refrigeration Technology
for the
Appliance Research Consortium

ABSTRACT

With the phase-out of CFC-12, the use of HFC-134a and polyolester (POE) oil became the preferred refrigerant/oil combination for the refrigerator appliance industry. Reliability data for this refrigerant/oil combination was minimal and initial testing showed a propensity for the capillary tubes to clog with a variety of contaminants. A test was designed by an industry group to accelerate the process of contamination and capillary plugging. This paper presents capillary tube stress test data that was developed for this group by it's member companies. This study investigated the relationship between capillary tube restriction levels and variables including compressor type, oil type, chlorine level and moisture level. Analysis of the contaminants included a visual description, infra-red spectroscopy, scanning electron microscope examination, measurements of total chlorine content and non-condensable gas content of the refrigerant. Oil samples were measured for moisture level, dissolved iron, total acid and an infra-red spectral analysis was performed.

INTRODUCTION

Production of CFC-12 ceased at the end of 1995. This precluded use of a material that was integral to the high reliability that had become synonymous with the refrigerator and forced the industry to screen and select alternate combinations of refrigerant and oil for reliability and wear characteristics.

Chemical refrigerant issues

CFC-12, as a chlorinated solvent, acted as a cleaning agent in the system to prevent deposition of higher molecular weight materials such as paraffinic processing grease and potassium carboxalate in the refrigerator-freezer capillary tubes.

Partial blockage of the capillary tube causes the run time to increase with little impact on the freezer and fresh food temperatures. However, a major blockage will significantly reduce the capacity and efficiency of a refrigeration system. With high usage, the compartment temperatures will increase and could necessitate a service call.

There are a variety of materials and mechanisms associated with capillary tube restriction. As the temperature of the liquid refrigerant in the capillary tube decreases due to the latent energy associated with the refrigerant phase change and heat transfer with the suction line, the solubility of most materials in 134a decrease and they precipitate out. The location of precipitation is dependent on the relative solubility of the material. Carboxylic acids from either brazing flux or high temperature reaction products from ester oil have very low solubility and therefore tend to precipitate out at the beginning of the capillary tube. Mineral oil, silicone oil and other light oils tend to come out later in the capillary tube. Small wear particles tend to flow through the capillary tube until they encounter the sticky greases or precipitated reaction products.

Operating pressures for R134a are greater than that of R12 systems. This requires more restriction for the expansion device to provide increased separation in pressures. Therefore, the diameter of the capillary tube is reduced in many

cases to provide for the required restriction. This increases the likelihood of capillary tube plugging since there is less cross-sectional flow area to accommodate contaminants.

Tight bends also tend to concentrate contaminants since the refrigerant will flash at these locations, thus reducing the liquid refrigerant temperature and corresponding solubility.

Compressor wear issues

CFC-12 acted as a lubricity agent in the compressors because the relatively chemically reactive chlorine formed a surface coating on the metal wear surfaces. Phosphate additives were also commonly used as metal passivators in CFC-12 systems. With the introduction of 134a it was necessary to remove the phosphates from the oil since the phosphates were found in the capillary tube blockages. It became necessary to find alternate methods for mitigating the effects of compressor wear. The industry had rejected mineral oil, commonly used with R12, due to it's low solubility with R134a. The synthetic lubricant polyolester (POE) was selected as its replacement in hermetic refrigerator applications.

Industry project R92-2

Several members of the refrigerator industry agreed in 1992 to establish a project which would identify the mechanisms contributing to the capillary tube blockage and the subsequent product failures resulting from the use of non-CFC refrigerants and compatible lubricant. This required the committee to design and perform tests which would accelerate the process of contamination and deposition of materials in the capillary tube. This test would be designed to be indicative of the service that a refrigerator would see in the field and measure the relative effect of the contaminants on performance.

The test procedure presented below and the associated data developed as part of project R92-2 was used by the member companies to qualify new designs. Typically, additional testing was performed by the refrigerator manufacturers and compressor suppliers to further qualify the designs.

Many subsequent improvements in processes and specifications have been made at each of the member companies which resulted in significant reductions in capillary tube plugging beyond the data presented here. Although the data presented may represent successful qualification for many of the designs tested, this data should not be taken to be typical of current production.

STRESS TEST PROCEDURE

Three organic chloride contaminant levels found in commercial R-134a would be used for the test. These were:

Cl^- less than 50 part per million (ppm);
Cl^- less than 200 ppm ± 40; and
Cl^- 500 ppm ± 40

The composition of the organic chlorides used to contaminate the R134a samples would only be specified for the 200 and 500 ppm samples. This would be a generic mixture of 25% R-114, 25% R-114a, 25% R-124 and 25% R-133a. Moisture levels were established at 100, 200, and 400 ppm ±40 ppm. H_2O ppm is defined as the total system moisture divided by the mass of the oil and refrigerant.

In January 1995, industry members were surveyed to determine conditions appropriate for the accelerated life stress test. The suggested conditions are listed below:

Motor winding temperature	270 ± 5 °F
Condenser mid Temperature	130°F ± 9°F
Capillary tube size	.026 ± .001 in.
Capillary in temperature	119°F to 126°F
Capillary out temperature	less than -20°F
Suction temp 6 inches from compressor shell	90°F to 110°F

duration	continuous run 3 weeks at 110°F followed by 1 week at 90°F
Dryer	3 Angstrom molecular sieve for 134a

After the system has been run under these conditions the suction/capillary tube assembly is removed and the flow rate through the capillary tube is measured using a wet test gas meter or rotometer. The measurement is determined with nitrogen gas flowing through the capillary tube with an inlet pressure of 100 psia. The measurement is conducted twice for each capillary tube and the average is used to calculate the volumetric flow rate.

After the flow has been checked, the capillary tube along with the dryer, compressor, compressor oil and refrigerant are removed for chemical analysis. The capillary tube is flushed with chloroform, which is assumed to remove most if not all of the residue. Then, the residue is analyzed and the capillary tube flow rate is measured again.

Flow rates after stress testing and solvent flushing are compared to calculate percent restriction of the capillary tube.

EQUIVALENT LIFE ESTIMATION

The purpose of the industry study was only to identify mechanisms contributing to the capillary tube blockage. The study was not designed to predict life of the product in the home. A simplified analysis can be made to better understand the rate of capillary tube plugging by assuming that temperature is the primary variable in predicting the life of the refrigerator. In fact, many other factors including system operating pressure, wear, and cleanliness of the manufacturing process determine the success of 134a implementation.

It is assumed that temperature accelerates chemical reactions that produce by-products which subsequently collect in the capillary tube. Chemical reaction rates are modeled by the Arrhenius equation which estimates a reaction rate at the application temperature from reaction rate data obtained at higher temperatures. For this analysis it is assumed that the reaction is driven by the temperature at the compressor windings which are elevated to 270°F during the test.

Arrhenius Model [4]:

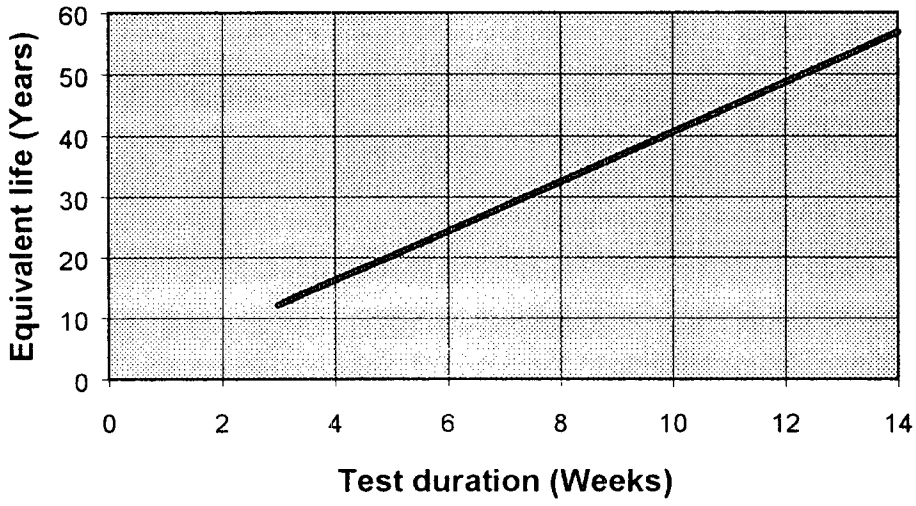
$$A_f = e^{\frac{Ea}{B}\left[\frac{1}{Tu} - \frac{1}{Ta}\right]}$$

Where
A_f acceleration factor
T_u application temperature in Kelvin, K
T_A temperature in the accelerated test, K
$B=8.623\times10^{-5}$ eV/K, Boltzman's constant
Ea is a factor determined experimentally, a value of 1.0 is assumed [5]

The number of years of equivalent life is calculated by dividing the acceleration factor by the percent runtime for the typical refrigerator. A runtime of 50% is used for the example in figure 1.

Figure 1 shows the equivalent life as a function of test duration based on the Arrhenius Model. An average compressor winding temperature of 155°F was used. This would be typical of a compressor operating in 70°F ambient condition.

Figure 1 Equivalent life vs Test duration



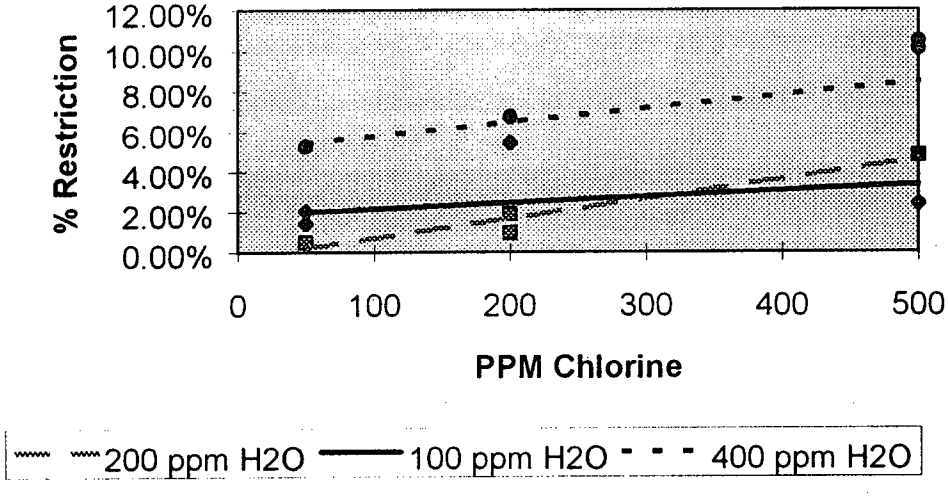
ANALYSIS OF TEST RESULTS

Tables 1 & 2 shows the results of the capillary tube blockage study sorted by increasing moisture level. Column 2 shows the compressor type. Each number represents a different manufacturer of the compressor. Similarly column 2 shows the oil type, representing the manufacturer of the oil used for the test. Typically a manufacturer will use a combination of these for a particular plant or assembly line. The data in this form shows a mild correlation between capillary restriction and the contaminant. However, the correlation becomes stronger when the data is sorted for the specific combination of compressor and oil. This will also filter out differences in lab procedure since the combination of compressor and oil uniquely identifies a originator of the test.

An example of the improved correlation can be seen when the combination of compressor 3 and oil A is used. The duration of the tests was 6 months. In figure 2, one can see that there is a general trend toward increased restriction with increased Chlorine level. The data is identified for H_2O level.

When the same data is plotted vs. Water content and identified for Cl level (Figure 3), one can see that there is a trend toward increased restriction with increased water content even though the systems used in the study contained a filter/drier.

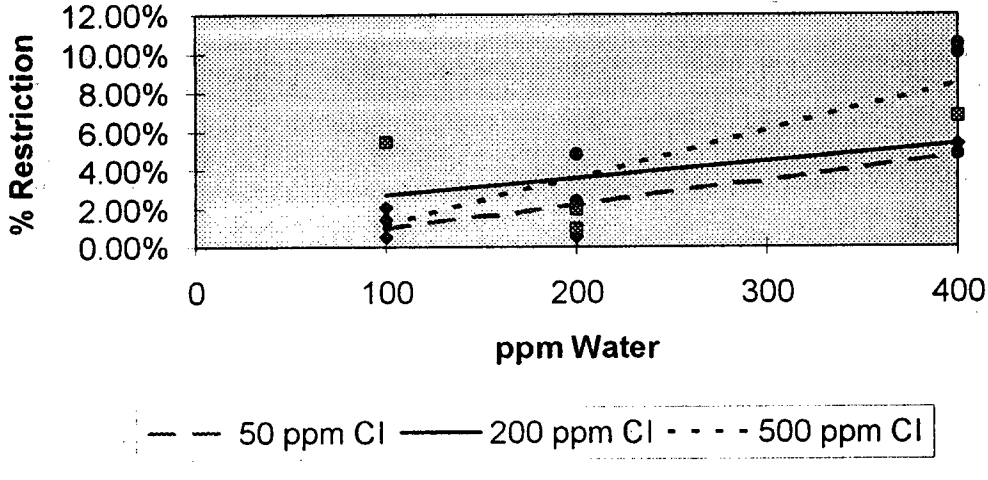
Figure 2 - PPM Organic Chlorine vs. % Restriction



Further analysis of the refrigerant in these cases shows that the Chlorine levels retrieved from the completed test correlated very closely with the levels injected at the start of the test.

However the water levels were severely reduced from the initial levels of up to 400 ppm to less than 15 ppm. This is to be expected. since the molecular sieve material would absorb moisture to this level.

Figure 3 - Moisture Level vs. % Restriction



FAILURE CASE STUDY

Additional work was performed to validate the maximum temperature for the stress test. This work was not part of the original industry work.

Table 3 shows three systems that failed stress test. The tests were running at a 79°F ambient for 30 days. During the first 27 days, the compressor shell temperature operated between 250 and 260°F resulting in a winding temperature between 275 and 285°F. In order to achieve these temperatures and enhance failure the air-side of the condenser in the circuit was insulated. It should be noted that this would represent an unrealistically harsh field condition.

When the capillary from sample 95, with 39.4% restriction, was flushed with chloroform 22.9 mg of a solid black residue was collected. Using infrared analysis, the residue was determined to be carboxylic acid salts from decomposed ester oil. The excess heat applied to this unit is suggested to be responsible for the decomposition of ester lubricant molecules. During the process of stress testing the freezer temperature increased from -5 to 5°F. This suggests that the blockage of the capillary tube restricted the refrigerant flow causing the freezer temperature to increase. Also, it was found that the 134a refrigerant contained about 10 ppm moisture. About 68 ± 3 ppm and 8.3% moisture was present in the ester oil and dryer, respectively. These values suggest the dryer still had remaining capacity. The oil acidity measured suggests that, for the most part, the oil was intact after stress testing.

Sample 94 with 14.6% restriction and sample 96 with 17.2% restriction were each split open exposing the contaminants in the tubing. Solid residues were concentrated at the inlet of the capillary tube. Residue at the inlet suggests the contaminant salt is highly insoluble since slightly insoluble residue has a tendency to be recovered near the capillary tube outlet. There was no visible residue at the capillary tube outlet. Infrared spectroscopy was used to determine that the residue was decomposed ester oil similar to that found in sample 95. The specific type of ester is unknown.

The oil from all three units were analyzed for metal. Each oil sample showed measurable amounts of iron, silicon, boron, and phosphorus. Boron is a component of brazing flux. The rest of the materials, which were present in very small amounts, can be attributed to either wear in the compressor or the machining processes used to manufacture the compressor and heat exchangers.

The oil removed from sample 96 was black instead of the typical yellow/straw color of ester oil. A large amount of aluminum found in this oil sample. Further analysis by the compressor supplier showed significant compressor wear in a temperature sensitive part.

Data from the stress test is summarized in table 3.

Table 3. Study of Three Failure Cases

	Sample 94	Sample 95	Sample 96
Test Days	30	30	30
Ambient Temp. (°F)	79	79	79
Frz Temp at 27th Day	-6	-5	-6
Frz Max Temp after 27th Day	2	5	11
Comp Temp at 27th Day	262	255	248
Comp Max Temp after 27th Day	282	280	272
Blockage (%)	15	39	17
Moisture in R134a (ppm)	23±1	10±0	12±1
Moisture in Oil (ppm)	27±2	68±3	18±3
Oil Acid Number (mg KOH/gm)	0.01	0.03	0.01
Dryer LOI (% moisture)	8.4	8.3	8.2

EFFECT OF CAPILLARY BLOCKAGE

Domestic refrigerators designed for the U.S. market are driven by the need to meet DOE energy consumption standards in addition to the performance requirements that customers have come to expect in this appliance. These products are typically optimized for minimum energy consumption by determining the capillary tube dimensions and the refrigerant charge which consumes the least energy. The refrigerator thermostat controls the on/off cycles of the

compressor to produce the desired temperature in both the fresh food and freezer compartments. If a large capillary tube restriction occurs the condensing pressure increases and the mass flow through the capillary tube is reduced thereby increasing compressor watts and run-time. The controls will continue to cycle the compressor to maintain acceptable temperatures in the fresh food and freezer compartments.

However, with larger restrictions, the compressor will eventually run 100 percent of the time. Freezer and fresh food temperatures will increase until a service call results. The degree of the effect on customer satisfaction is dependent on the ambient operating conditions. In areas of the country that require more reserve cooling capacity this could occur with capillary flow restrictions as low as 20 percent.

Although each of the manufacturers participating in the industry sponsored study have their own requirements for reliability testing, it is generally accepted that designs should result in less than 10 percent capillary blockage after 6 months. This will typically result in a plateau in a plot of restriction vs. time suggesting stable operation with no increase in restriction beyond the 6 month test period. In addition, compressor suppliers perform accelerated reliability testing to ensure acceptable lifetime in the field.

CONCLUSIONS

This paper described a test which was designed by an industry sponsored group accelerate the process of contamination and capillary plugging. Capillary tube stress test data was presented and a study investigating the relationship between capillary tube restriction levels and variables which include compressor type, oil type, chlorine level and moisture level was performed. The analysis of the contaminants included a visual description, infra-red spectroscopy, scanning electron microscopic examination, measurements of total chlorine and non-condensables in the refrigerant. Oil samples were measured for moisture level, iron content, total acid measurement and an infra-red spectral analysis was performed.

Capillary tube plugging increases with increased refrigerant chlorine levels.

Capillary tube plugging increases with increased moisture level in the refrigeration system.

Measurable restrictions for the contaminated units occur after a three to four week stress test with a compressor shell temperature under 250°F. The residue causing capillary tube blockage was found to be the added contaminants mixed with ester oil breakdown products and salts.

Clean systems produced slightly lower levels of capillary tube restriction and residue than the deliberately contaminated systems. No ester lubricant decomposition was seen in clean system.

Very little correlation existed between the system refrigeration capacity and the degree of capillary tube plugging. This may be due to the degree of experimental error in the capacity measurement. Several of the units were operating in poorly controlled ambient conditions.

The failure case study shows a 39.4% blockage with 22.9 mg of residue after 30 days of stress test. Elevated temperature and moisture levels enhanced the decomposition of ester oil. Capillary tubes contained a large quantity of carboxylic acid salt at the inlet and the compressor showed significant wear.

It is believed that the POE oil and/or compatible process oils that exist in the system may be decomposed when compressor shell temperature exceed 250°F. This process is aggravated when the system contains moisture and other foreign residue.

ACKNOWLEDGMENT

The support of AHAM and the members of the Refrigeration Technical Advisory Committee is gratefully acknowledged.

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Table 1 - Capillary Tube Blockage Analysis, R92-2

Unit	Compr	Oil	Months	Moisture	Organic	Freezer Capacity Temp			Capillary Flow (SCFM)			Cap Tube Residue Analysis	
ID #	Type	Type	On Test	(ppm)	Cl (ppm)	Before	After	Change	Before	After	Change	Visual Assessment	IR
40	3	C	1	100	50	-8.8	-17.4	9.9%	.219	.219	0.0%	Beige Solids	Ester oil and Mineral oil
49	3	C	1	100	50	N/A	N/A		.221	.221	0.0%	Beige Solids	Ester oil and Mineral oil
50	3	C	1	100	50	-.6	-2.4	1.5%	.219	.219	0.0%	Beige Solids	Ester oil
43	3	C	1	100	50	1.4	-6.9	10.8%	.221	.220	-0.5%	Beige Solids	Ester, Min. & Silicone oil, and Chlor.
28	3	A	6	100	50	.0	-3.0	2.7%	.208	.207	-0.5%	CHCl3 flush very dark	ester lubricant
45	3	C	1	100	50	-10.7	-16.2	6.2%	.215	.213	-0.9%	Beige Solids	Ester oil and Mineral & Silicone oil
22	1	A	9	100	50	-13.5	-14.6	1.1%	.228	.225	-1.3%		
29	3	A	6	100	50	.0	-1.0	0.9%	.208	.205	-1.4%	CHCl3 flush very oily	ester lubricant
20	3	A	6	100	50	-11.0	-9.1	-1.9%	.238	.233	-2.1%		
52	3	C	1	100	50	5.7	6.9	-1.0%	.223	.216	-3.1%	Beige Solids	Ester oil and Silicone oil
51	3	C	1	100	50	4.6	4.5	0.1%	.212	.205	-3.3%	Beige/Brown Solids	Ester oil and Silicone oil
24	3	B	6	100	50	-10.8	-10.3	-0.5%	.231	.219	-5.2%		
46	3	C	1	100	50	-7.4	-12.8	6.3%	.221	.208	-5.9%	Beige Solids	Ester oil and Mineral oil
55	1	B	1	100	50	-3.9	-2.3	-1.4%	.147	.137	-6.4%		
26	1	B	9	100	50	-13.5	-14.1	0.6%	.237	.210	-11.4%	White Powder	Aliphatic ester with aliphatic
32	3	A	6	100	200	.0	2.0	-1.8%	.220	.208	-5.5%	CHCl3 flush very oily	ester lubricant
54	1	B	1	100	200	-4.2	-4.4	0.2%	.147	.138	-6.1%		
1	1	A	9	100	350	-4.6	-5.0	0.3%					S&C oil,par,Ksalt
6	2	B	9	100	350	-6.2	-6.1	-0.1%					S&C oil,par,Ksalt,mol sieve
12	2	A	9	100	350	-8.0	-8.8	0.7%					S&C oil
18	1	B	9	100	350	-5.5	-6.1	0.5%					C oil,Ksalt
36	3	A	6	100	500	.0	-1.0	0.9%	.209	.204	-2.4%	CHCl3 flush - oily	ester lubricant
53	1	B	1	100	500	-6.5	-6.2	-0.3%	.147	.135	-8.3%		
4	2	A	9	100	700	-7.4	-6.1	-1.1%					C oil par
14	2	B	9	100	700	-7.6	-7.9	0.3%					C oil,mol sieve
16	1	A	9	100	700	-5.8	-6.2	0.3%					C oil
30	3	A	6	200	50	.0	-1.0	0.9%	.208	.207	-0.5%	CHCl3 flush trace amount	ester lubricant
34	3	A	6	200	200	.0	-5.0	4.5%	.208	.206	-1.0%	CHCl3 flush oily	ester lubricant
33	3	A	6	200	200	.0	.0	0.0%	.210	.206	-1.9%	CHCl3 flush	ester lubricant
3	1	B	9	200	350	-5.6	-4.7	-0.8%					S&C oil,par,Ksalt,mol sieve
5	2	A	9	200	350	-7.4	-4.9	-2.1%					C oil par
15	2	B	9	200	350	-8.0	-7.4	-0.5%					C oil,mol sieve
17	1	A	9	200	350	-6.8	-6.7	-0.1%					C oil
37	3	A	6	200	500	.0	8.0	-7.3%	.208	.198	-4.8%	CHCl3 flush	ester lubricant
2	1	A	9	200	700	-5.6	-5.4	-0.2%					S&C oil,par
7	2	B	9	200	700	-6.4	-6.0	-0.3%					S&C oil,par,Ksalt
13	2	A	9	200	700	-5.4	-5.9	0.4%					S&C oil,mol sieve
19	1	B	9	200	700	-7.7	-7.8	0.1%					C oil,Ksalt
41	3	C	1	250	50	-9.1	-14.2	5.9%	.219	.219	0.0%	Beige Solids	Ester oil and Chlorine
47	3	C	1	250	50	-4.0	-10.8	8.3%	.231	.231	0.0%	Beige Solids	Ester oil
8	2	A	9	250	350	-5.6	-4.3	-1.1%					S&C oil,par
10	2	B	9	250	350	-3.9	-3.7	-0.2%					C oil,mol sieve
9	2	A	9	250	700	-6.2	-5.5	-0.6%					S&C oil,par
11	2	B	9	250	700	-3.8	-5.1	1.1%					?
48	3	C	1	300	50	3.8	4.0	-0.2%	.218	.216	-0.9%	Beige Solids	Ester oil
42	3	C	1	300	50	-0.9	-7.5	8.4%	.215	.213	-0.9%	Beige/Brown Solids	Ester oil
44	3	C	1	300	50	-19.0	-8.7	-10.6%	.223	.219	-1.8%	Beige/Brown Solids	Ester oil
31	3	A	6	400	50	.0	-2.0	1.8%	.208	.197	-5.3%	CHCl3 flush	ester lubricant
35	3	A	6	400	200	.0	47.0		.208	.194	-6.7%	CHCl3 flush	ester lubricant
25	3	B	6	400	500	-10.0	-9.6	-0.4%	.238	.227	-4.4%		
39	3	A	6	400	500	.0	-1.0	0.9%	.208	.198	-4.8%	CHCl3 flush oily	ester lubricant
23	1	A	9	400	500	-13.7	-14.2	0.5%	.236	.216	-8.7%	White Powder	Aliphatic ester w/min oil (>#2)
38	3	A	6	400	500	.0	2.0	-1.8%	.208	.187	-10.1%	CHCl3 flush oily	ester lubricant
21	3	A	6	400	500	-11.9	-10.8	-1.1%	.240	.215	-10.5%	White & Black Material	Aliphatic ester w/mineral oil
27	1	B	N/A	400	500	-12.6	N/A		.229	N/A			

Table 2 - Capillary Tube Blockage Analysis, R92-2

Unit	Cap Tube Residue Analysis		Refrigerant Sample			Oil Sample			
ID #	SEM/AA/DCP (elemental)	Other Particulate	Total Cl	NCG %	Other	H2O ppm	Fe ppm	TAN	IR
40	N/A	Carboxylic acid salt	N/A	-	22 ± 1 H2O	18 ± 3	4	0.01	Ester oil
49	N/A	Carboxylic acid salt	N/A	-	28 ± 2 H2O	8 ± 2	1	0.01	Ester oil
50	N/A	Carboxylic acid salt	N/A	-	16 ± 3 H2O	20 ± 2	5	0.02	Ester oil
43	N/A	Carboxylic acid salt	N/A	-	24 ± 0 H2O	23 ± 2	2	0.02	Ester oil
28	XRF - Fe, Cu, Si, S, K		0 ppm	0.8	tr R-124/114a	8	0	0.03	1.1
45	N/A	Carboxylic acid salt	N/A	-	26 ± 1 H2O	30 ± 1	5	0.01	Ester oil
22									
29	XRF - Fe, Cu, Si, S, K		4	0.5	tr R-124/114a	4	0	0.04	1.9
20									
52	N/A	Carboxylic acid salt	N/A	-	20 ± 0 H2O	9 ± 1	8	0.02	Ester oil
51	N/A	Carboxylic acid salt	N/A	-	15 ± 1 H2O	11 ± 2	7	0.01	Ester oil
24									
46	N/A	Carboxylic acid salt	N/A	-	32 ± 7 H2O	14 ± 3	7	0.01	Ester oil
55									
26	Si,C,O,Al,S,K,Ca,Fe,Cu	High MW HC,tops ~975							
32	XRF - Fe, Cu, S, K		184	0.25	-	11	3	0.04	1.8
54									
1	Cl,Cu,S,Si,K,Ca,Al,O			0.96		8		0.034	
6	Cu,S,Cl,Al,K,O,Si,Fe			1.19		7.1		0.008	
12	Cu,Cl,Na,K,S,Ca,Al,P,Fe,Ti,Si		No Change			9		0.056	
18	Cu,Cl,K,S,Al,Fe,Si,P,Ca		No Change			14.6		0.016	
36	XRF - Fe, Cu, Si, K		439	0.5	-	6	3	0.05	6.9
53									
4	Cu,S,Cl,Al,K,O,Si			1.45		2		0.032	
14	Cu,Cl,K,S,Al,Fe,Si,O		No Change			NA	2.02	0.047	
16	Cu,Cl,K,S,Al,P,Fe,Ti,Si,Zn,O		No Change			9.4	4.63	0.024	
30	XRF - Fe, Cu, Si, S		0	1	tr R-124/114a	12	0	0.05	1.9
34	XRF - t-Fe, Cu, S, K		172	0.4	-	8	2	0.04	2.4
33	SEM - Fe, Al		177	0.4	-	11	9	0.05	4
3	Cl,Cu,S,Si,K,Ca,Al,O,Fe			1.09		3.9	0.18	0.003	
5	Cu,S,Cl,Al,K,O,Si			1.2		6	0.36	0.023	
15	Cu,Cl,K,S,Al,P,Fe,Ti,Si,Zn,O		No Change			11.9	1.87	0.031	
17	Cu,Cl,K,S,Al,Fe,Si		No Change			7.5	2.68	0.027	
37	SEM - Fe, Al, Cl		482	-	-	12	4	0.05	7.8
2	Cl,Cu,S,Si,K,Ca,Al,O			0.95		6.7		0.019	
7	Cu,S,Cl,Al,K,Si,Fe			NA		7.8	0.96	0.01	
13	Cu,Cl,K,S,Al,Fe,Si,O		No Change			14		0.051	
19	Cu,Cl,K,S,Al,Fe,Si,Zn		No Change			6.8		0.036	
41	N/A	Carboxylic acid salt	N/A	-	34 ± 1 H2O	22 ± 2	1	0.01	Ester oil
47	N/A	Carboxylic acid salt	N/A	-	28 ± 0 H2O	25 ± 3	1	0.01	Ester oil
8	Cu,S,Cl,Al,K,O,Si,Fe			1.15		3.7		0.013	
10	Si,O,Cu,Al,Cl,S,Ca			0.47		7.7		0.003	
9	Si,O,Cu,Al,Cl,S			0.78		2		0.016	
11	Si,O,Cu,Al,Cl,K			0.68		6.7		0.052	
48	N/A	N/A	N/A	-	22 ± 1H2O	14 ± 2	1	0.02	Ester oil
42	N/A	N/A	N/A	-	22 ± 3 H2O	26 ± 3	3	0.01	Ester oil
44	N/A	Carboxylic acid salt	N/A	-	20 ± 6 H2O	14 ± 2	2	0.01	Ester oil
31	SEM - Fe, Al		6	0.5	tr R-124/114a	7	0	0.04	1.8
35	SEM - Fe, Al, K, Cl	High-side Leak, wear on con-rod	252	0.4	-	9	0	0.05	3.6
25									
39	XRF - Fe, Cu, Si, S, K		478	-	-	8	2	0.06	2.8
23	C,O,Al,Si,S,Cl,K,Fe,Cu,Zn	High MW HC,tops 956							
38	SEM - Fe, Al, K, Cl	wear observed on con-rod	474	-	-	5	0	0.06	9.1
21	Al,Si,K,Fe,S,Cl,Cu,O	High MW HC,tops ~871							
27									

Performance of refrigerators retrofitted with HFC-134a and HC blend.

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INTRODUCTION

According to the Montreal Protocol, CFCs has been phased-out by 1st January 1996 in the developed countries and should be phased-out by 2010 in the developing countries. Indian household refrigerators still use CFCs and there is a significant amount of effort needed to phase-out CFCs in this sector. There are already over 13 million refrigerators operating with CFC-12. During the transition period, many more new ones will be installed to meet the growing demands. The life of these refrigerators will extend much beyond these phase-out dates.

The choice of alternative refrigerants to CFC-12 is today narrowed down to two candidates, namely, HFC-134a and Hydrocarbons. Therefore, it is of a great interest to assess the performance of refrigerators with these alternative refrigerants under retrofit conditions. This is to examine whether the life of these refrigerators can be conveniently extended and their performance is within the acceptable limits. If found suitable, this will be an attractive option economically as the Montreal Protocol does not compensate the consumers for the incremental cost to phase-out CFCs. For many families, a refrigerator is a life time purchase and, very often, it is repaired rather than replaced by a new one.

This study examines the energy consumption of a typical 165 l retrofitted with HFC-134a and HC-290/HC-600a (50%/50% by weight) according to IS 1476. Agarwal (1996), Devotta and Kulkarni (1996) and Schwank (1996) have discussed the issues related to the use of hydrocarbon blends in Indian refrigerators and their potential for countries operating under Article 5 of the Montreal Protocol. Therefore, the relative merits and demerits of one over the other are not discussed in this paper.

ENERGY CONSUMPTION OF INDIAN REFRIGERATORS

IS-1476, by the Bureau of Indian Standards, specifies many tests for the performance testing of domestic refrigerators. The major tests specified by this standard for testing the performance of a refrigerator are Door Seal Test, No-load Pull Down Test, Ice-Making Test, Door and Fitting Test, Pressure Test, Rated Energy Consumption Test, etc. But more importance is given generally to three main tests, namely, Rated Energy Consumption Test (No-Load Performance Test), No-Load Pull Down Test, Ice-Making Test as they deal with energy and performance.

Typically, a 165 l Indian refrigerator/ freezer, under laboratory test conditions of 32°C, consumes about 1.3 kWh/day equivalent to 0.78 kWh/ day/100 litre. This is much higher than the values set by current international standards. Approximately, all refrigerators currently in use in India put together consume not less than 750 MW of electricity. A conservative saving about 10% will mean a saving of 75 MW, saving of a capital of about 1500 crores for an equivalent

power station. This also means, on a conservative estimate, a saving of 5.5 million tonne of CO_2 emission into the atmosphere.

RATED ENERGY CONSUMPTION TEST : The purpose of this test is to lay down the maximum energy consumption per day, for a given capacity, under the standard conditions. The conditions to be set for carrying out this test are as follows:

(a) The ambient temperature is set at 32°C. (b) The operating conditions will be taken to be stabilized when over a period of two hours, the mean temperature measured at the same stage of the control cycle do not vary by more than 0.5°C from the regulated test. (c) The thermostat will be set at the position of the setting such as to obtain conditions (g) & (h). (d) The refrigerator will be run under no-load conditions. (e) The temperature at the geometric centre of the evaporator shall not exceed -5°C. (f) The mean internal temperature of the general storage compartment shall be 5°C. (g) The power consumption and the percentage running time shall be recorded for a period of six hours after stabilized conditions have been reached.

The rated energy consumption for refrigerators under test conditions shall not be more than the values specified below for the following rated capacity refrigerators.

(a) Up to 65 litres : 1.5 kWh per day
(b) 66 to 165 litres : 2 kWh per day
(c) 166 to 300 litres : 2.25 kWh per day.

Energy consumption for other rated capacities may be interpolated.

NO-LOAD PULL DOWN TEST : The purpose of this test is to check the no load characteristics of the refrigerating unit, i.e., pull-down time, the no load power consumption and the percentage running time. The conditions to be set for carrying out this test are as follows :

(a) Ambient temperature is set at 43°C. (b) The refrigerator is kept open and soaked for about 24 hours for getting the stable temperature throughout the refrigerator. (c) The refrigerator door is then closed and the refrigerator is allowed to run either with the thermostat kept at the maximum position or it is taken out of the circuit. (d) The time taken to pull the (mean) temperature of the fresh food compartment from 43°C to 7°C and the energy consumed during this period are to be recorded. (e) If the refrigerator cycles, then the percentage running time also should be recorded. (f) After attaining the stable operating conditions, the average temperature in the fresh food compartment should not be above 7°C.

The following data are reported: (a) Pull down time - The time required to pull down the mean fresh food compartment air temperature from 43°C to 7°C. (b) Pull down energy consumption - The energy consumption required to pull down the mean cabinet air temperature from 43°C to 7°C. (b) Power consumption for 6 hours. (c) The percentage running time, if the compressor starts cycling.

ICE-MAKING TEST : The purpose of this test is to check the ice making capability of the refrigerator as to the time required and the energy consumption. Following are the conditions for conducting the ice making test.

(a) Ambient temperature should be 43°C. (b) The thermostat shall be set in the coldest or

maximum position and stable operating conditions should be obtained before starting the test. (c) Two ice trays of 250 ml each shall be filled with water up to a level within 5 mm from the top and promptly placed in the evaporator compartment. (d) The water temperature in the ice tray when placing the tray into the evaporator compartment, shall be 30 ± 1°C. (e) After the stable operating conditions are obtained, the test shall be continued until the freezing of water in the trays takes place.

The following data are reported: (a) Total time required to make ice. (b) Total energy consumed during the test. (c) The percentage running time.

The refrigerator performance test room at NCL, Pune, has been designed as per IS-1476. It is provided with a constant temperature room, a control panel and a data logger/ data acquisition system with a computer interface.

PROCEDURE FOR RETROFITTING

In this study, retrofitting was done from CFC-12 to HFC-134a and a hydrocarbon (HC-290/HC-600a) mixture according to the following procedure. This procedure was evolved from various published reports and from various manufacturers of HFC-134a and POE lubricating oils.

HFC-134a : In this study refrigerators manufactured with CFC-12 are used for the retrofitting. The compressor is removed from the refrigerator and the original oil is drained and then charged with the POE oil grade (ISO VG 32), recommended for HFC-134a. The compressor is independently run dry for a few minutes and the oil is then drained. This is to make it free from any incompatible materials used during the manufacturing as well as the mineral oil and residual CFC-12. This is repeated at least twice to ensure the removal of all non-compatible materials, like the mineral oil and CFC-12, from the compressor. Then the compressor process tubes are closed with caps to avoid any entry of air or moisture. The condenser coil and evaporator heat exchanger are cleaned with either petroleum ether or pentane followed by nitrogen flushing. This is very important to remove CFC-12 and the mineral oil retained within these components and to make the system as dry as possible. Similar to the compressor, the tube ends are closed with caps. The original filter dryer used for CFC-12 is replaced by a filter dryer compatible with HFC-134a. The capillary length is also increased by 10% by adding an appropriate length to the existing capillary lengths. Two pressure gauges, with appropriate ranges, are fitted to the suction and discharge lines to monitor the suction and discharge pressures. The compressor is fitted back to the refrigerator and nitrogen is charged to maintain a pressure of 8 bar. The system is kept under pressure with nitrogen for 24 hours. Then all the joints are tested for leak by using soap solution. If there is no leak as indicated by the soap solution test and the pressure within the refrigerator is maintained for about 24 hours, the system is then evacuated for about 5 hours to ensure dry and moisture free system. HFC-134a is then charged through the suction side of the compressor while it is running. The quantity of HFC-134a charged is approximately 95% of the original charge of CFC-12 in the refrigerator. In this way the two different brands of 165 l refrigerator were modified and retrofitted from CFC-12 to HFC-134a.

HC Mixture : Almost identical procedure is followed for the HC mixture except that no changes in the capillary length and filter dryer were done. Although the same mineral oil is used with hydrocarbon, the oil change is done to ensure the removal of residual CFC-12 from the

refrigerator. One major difference for the mixture is with respect to charging. For a mixture, it is essential to draw the refrigerant as liquid to ensure that there is no change in the refrigerant composition occurs while charging. If a dip tube is provided in the cylinder, then the cylinder may be kept in an upright position while charging. Otherwise, the cylinder has to be kept in an inverted position. A few turns of a capillary coil may be attached between the cylinder and the suction port and the flow rate may be kept slightly lower than the normal to ensure full vaporisation takes place before the refrigerant enters the compressor. The amount of refrigerant charge is about 40-45 % of the original charge of CFC-12. Similar to that of HFC-134a, two different brands of 165 l refrigerator were retrofitted with the HC mixture. Since the amount of charge is very less to CFC-12, it is advisable to charge the hydrocarbon mixture by weight rather than by pressure.

RESULTS AND DISCUSSION

The results for rated energy consumption test, pull down test and ice making test are presented in Tables 1 and 2 for Brand I and Brand II refrigerators respectively.

It can be seen from Table 1 that, for Brand I refrigerator, the energy consumptions for CFC-12 and HC mixture are comparable while for HFC-134a, it is about 3.8% higher. For CFC-12 and HC mixture, the thermostat setting is able to achieve the required temperature conditions closely. However, for HFC-134a, the thermostat setting has to be set at a higher position in order to fulfil the condition in the freezer although the prescribed temperature conditions in the fresh food has been achieved already. It appears that, if the thermostat is adjusted, it may be possible to bring down the energy consumption even for HFC-134a. The percentage compressor running times for all three cases are more or less the same although it is the highest for HFC-134a.

An analysis of the pull down test results for Brand I reveals that the final freezer temperature and fresh food compartment temperatures are very much reduced when the refrigerator is retrofitted either with HC mixture or HFC-134a. Therefore, retrofitted refrigerators required much longer pull down time and higher energy consumption. This also means that there is a significant fall in the cooling capacity of a CFC-12 compressor at 43°C when retrofitted with HC mixture or HFC-134a. It should be possible to improve the performance by appropriate optimisation measures including capillary length adjustment and refrigerant charge.

The ice making times for all three refrigerants are almost the same although it is marginally lower for CFC-12 and marginally higher for HC mixture. The energy required is the least for CFC-12 while it the highest for HC mixture. This is similar to the pull down test and the same reasons are valid for these results as well.

From Table 2, it can be seen that Brand II refrigerator with HFC- 134a requires the higher energy consumption while there is a reduction for HC mixture with respect to CFC-12. With CFC-12, the thermostat had to be kept at a higher position in order to achieve the required temperature conditions in the fresh food compartment. It appears that, during the design of Brand II refrigerator, more emphasis is given for retaining the cold within the freezer box (by providing a door and restricting the air flow from the inner part of the freezer box to the fresh ffod compartment). This results in colder temperature in the freezer than that is normally required. However, such a design results in the energy penalty as per the standards. Adjustment of the

thermostat band may result in better energy performance under retrofitted conditions.

In the pull down tests for Brand II, the final temperature in the freezer is higher under retrofitted conditions and there are energy penalties as well. However, the pull down time is the lowest for the HC mixture. Similarly, in the ice making tests, the HC mixture gives the best performance with the lowest energy consumption and with the shortest time.

In this study, the retrofitting procedure was restricted to the simple conversion with as little modification as possible. These performance characteristics may be improved with some optimisation procedures with different capillary lengths and refrigerant charge.

It may be noted that these retrofitted refrigerators have been running for the last 15 months. The Brand I refrigerator with the HC mixture has been running for more than 15 months without any problem. Similarly, the Brand I refrigerator with HFC-134a is also running for about 13 months. The Brand II refrigerator with HC mixture had some problem of leakage at the initial stage. Once this was rectified, the system is running continuously for more than 13 months. The Brand II refrigerator with HFC-134a initially ran for about 2 months and failed. After a careful observation, it was found that there was a considerable decrease in the suction pressure suggesting that there was some blockage within the system. This was confirmed by the Nitrogen pressure test. We replaced the dryer with a new one and recharged with HFC-134a. After four months there was again a considerable decrease in both suction and discharge pressures. This meant that some leak had occurred from the system. So, we went through the same procedure again and recharged the refrigerator. The Brand II refrigerator is running from mid February, 1997 without any problem.

CONCLUSION

The following observations can be made based on the experience from the present retrofit study :

(i) Better evacuation and leak testing practices have to be introduced. This is specially essential for both with HFC-134a because of its hygroscopic nature and with the HC mixture owing to its flammability. (ii) Accurate charging of refrigerant of smaller quantities is particularly a problem for hydrocarbons as the charge quantity is about 40-45% of the CFC-12 charge for the equivalent cooling capacities. There is a need to use a mini-charging station and smaller refrigerant gas cylinders, otherwise, there is a possibility of overcharging. (iii) Better service and tool kits have to be provided particularly to reduce the leakage problem. This is extremely important for flammable hydrocarbons and their blends. (iv) The current practices for electrical connections and power source points are not safe enough for hydrocarbons and there is a significant need to improve in this issue.

It can be concluded that the hydrocarbon mixture refrigerant is a most promising alternative working fluid for household refrigerators. This is free from any future controversies with respect to ozone layer depletion and green house effect. The performance of refrigerators with hydrocarbon mixture and HFC-134a may be almost similar with CFC-12 if the system is optimised. However, the safety aspects under retrofit conditions should be thoroughly investigated.

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TABLE 1 RESULTS OF BRAND I AS PER IS-1476

RATED ENERGY CONSUMPTION TEST

Ambient Temperature = 32°C

TEST PARAMETER	CFC-12	HC-Mix.	HFC-134a
Freezer Air Temperature (°C)	-5.1	-5.4	-5.5
Average Fresh Food Compartment Temperature (°C)	4.7	4.8	2.8
Energy Consumed for 6 hours (kWh)	0.446	0.443	0.461
Energy Consumed per Day (kWh)	1.78	1.77	1.84
Number of ON/OFF Cycles	24	20	26
Percentage Running Time (%)	55.55	53.61	57.87

PULL-DOWN TEST

Ambient Temperature = 43°C

TEST PARAMETER	CFC-12	HC-Mix.	HFC-134a
Freezer Air Temperature (°C)	-10.8	-6.8	-6.0
Average Fresh Food Compartment Temperature (°C)	1.6	4.9	5.4
Pull Down Time [43°C to 7°C] (Minutes)	130	176	180
Energy Consumed During Pull Down (kWh)	0.360	0.410	0.430
Energy Consumed For 6 hours (kWh)	0.769	0.820	0.826
Percentage Running Time (%)	100	100	100

ICE MAKING TEST

Ambient Temperature = 43°C

TEST PARAMETER	CFC-12	HC-Mix.	HFC-134a
Time Required to Make Ice (Minutes)	52	59	54
Energy Consumed (kWh)	0.125	0.147	0.135

TABLE 2 RESULTS OF BRAND II AS PER IS-1476

RATED ENERGY CONSUMPTION TEST

Ambient Temperature = 32°C

TEST PARAMETER	CFC-12	HC-Mix.	HFC-134a
Freezer Air Temperature (°C)	-8.2	-5.6	-5.4
Average Fresh Food Compartment Temperature (°C)	4.9	3.8	4.3
Energy Consumed for 6 hours (kWh)	0.424	0.427	0.456
Energy Consumed per Day (kWh)	1.690	1.668	1.82
Number of ON/OFF Cycles	19	16	19
Percentage Running Time (%)	58.63	61.67	59.55

PULL-DOWN TEST

Ambient Temperature = 43°C

TEST PARAMETER	CFC-12	HC-Mix.	HFC-134a
Freezer Air Temperature (°C)	-9.7	-8.5	-7.2
Average Fresh Food Compartment Temperature (°C)	3.5	3.8	2.6
Pull Down Time [43°C to 7°C] (Minutes)	157	148	162
Energy Consumed During Pull Down (kWh)	0.402	0.390	0.423
Energy Consumed For 6 hours (kWh)	0.830	0.874	0.868
Percentage Running Time (%)	100	100	100

ICE MAKING TEST

Ambient Temperature = 43°C

TEST PARAMETER	CFC-12	HC-Mix.	HFC-134a
Time Required to Make Ice (Minutes)	57	53	56
Energy Consumed (kWh)	0.138	0.129	0.132

Update on Mixture THR02 as a Long-Term Alternative to CFC-12 and HFC-134a

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ABSTRACT

A new refrigerant mixture THR02 based on CF_3I was proposed as a new long-term and "drop-in" alternative to CFC-12 and HFC-134a. It has zero ODP, low GWP value (<50), non toxicity, non flammability, near-azeotropic and good thermal performance. The thermal parameters of THR02 such as the operating temperatures, pressures and volumetric capacity are very close to those of CFC-12 and HFC-134a. Therefore, THR02 can be applied directly to existing and new equipments as "drop-in" alternative.

In this paper, the further evaluation results about reliability and thermal performance are discussed in detail. The miscibility of THR02 with MO, AB and POE oil is introduced. The material compatibility evaluations are presented. The composition change during refrigerant leakage out from cylinder has been tested. The thermal performance of domestic refrigerator using THR02 after two-years running is further discussed.

INTRODUCTION

Now the alternatives to CFC-12 are used in refrigerae applications. The leading alternative is HFC-134a, which has a GWP value about 1300 times higher than that of CO2. In addition, it has recently been reported that the breakdown of HFC-134a in the atmosphere generates triflur-acetic acid (TFA), which, according to current studies is not further broken down by light or hydrolysis, or biologically by plants or animals. TFA is a highly hygeoscopic corrosive liquid which is classified as harmful to health[1]. So HFC-134a seems not be a long-term refrigerant. The hydrocarbons have low GWP value and good miscibility with lubricant, but they are flammable.

We have found THR02 is a promise refrigerant as a long-term "drop-in" alternative to CFC-12. THR02 has the following characters[2,3]:

1. Environment Friendly

The mixture THR02 has zero ODP value, GWP≈50 (100 yrs, CO2=1; CFC-12=8500, HFC-134a=1300).

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2. Safety

Acute inhalation studies revealed that CF_3I has a low order of toxicity and its NOAEL and LOAEL value are similar to CFC-11. Therefore, THR02 can be acceptable in domestic refrigerators.

The composition of mixture THR02 is determined by flammability test to ensure non flammability of varied conditions such as different temperatures, normal operation, storage/shipping, after leakage conditions.

3. Thermophysical Properties

The maximum glide temperature among the pressure arrange of 0.1 to 2.0 MPa is less than 1.5°C. In practice, the glide temperature in evaporator and condenser is less than 1.0℃ respectively. So THR02 is a near-azeotropic refrigerant mixture.

The vapor pressure of THR02 is very similar to that of CFC-12. At the same time, the operating temperatures, pressures and volumetric capacity are very close to those of CFC-12. Therefore, THR02 can be applied directly to existing equipments as "drop-in" alternative.

4. Thermal Performance

The COP and q_V value are respectively equal to or higher than that of CFC-12.

POSSIBLE ALTERNATIVE TO HFC-134a

Analysis using the same method as to CFC-12, we found that THR02 may be an alternative to HFC-134a. In order to analysis and compare the thermodynamic performance of THR02 and HFC-134a, we have made the evaluation by calculating the refrigerate cycle properties.

The refrigerator working condition is: Te=-23.3 ℃, Tc=54.4 ℃, Tsub=32.2 ℃, Tsup=32.2 ℃, the ambient temperature is 32.2 ℃, the compressor efficiency assumed η_p=0.8. The automobile air-conditioner working condition is: Te=-1 ℃, Tc=62 ℃, Tsub=57 ℃, Tsup=9 ℃, the compressor efficiency assumed η_p=0.72. The calculating resultes are listed as Table 1.

Table 1. Cycle calculation results for HFC-134a and THR02

Working condition	Refrigerator		Automobile A/C	
Refrigerant	HFC-134a	THR02	HFC-134a	THR02
Pevap, MPa	1.15	1.16	2.82	2.73
Pcond, MPa	14.75	13.49	17.72	16.09
Pressure Ratio	12.9	11.6	6.29	5.89
Discharge Temp., ℃	134.9	151.5	91.4	103.2
Glide GTcond.		1.08		0.81
Temp., ℃ GTevap.		0.78		0.72
COP	1.00	1.05	1.00	1.08
q_o	1.00	0.93	1.00	0.98
q_V	1.00	1.04	1.00	1.05

The vapor pressure curves for THR02 and HFC-134a are showed in Figure 1.

From mentioned above, the COP of THR02 is higher than that of HFC-134a about 5% or 8% respectively in refrigerator or automobile A/C. The pressure and pressure ratio are lower than that of HFC-134a. The q_V of THR02 is equal to or slight higher about 5% than that of HFC-134a. So THR02 seems to be a "drop-in" alternative. Moreover, MO can be used for THR02 as following.

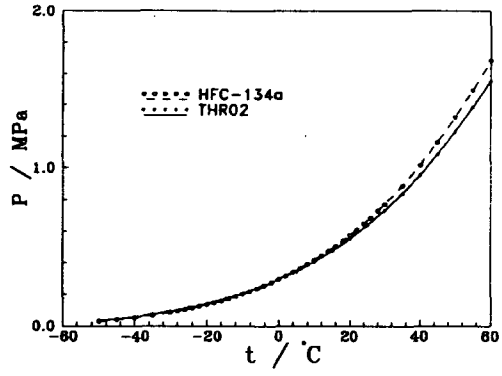

Fig.1 The Vapor Pressure Curves for THR02 and HFC-134a

MISCIBILITY WITH DIFFERENT OILS

THR02 is a possible alternative to CFC-12 and HFC-134a, so the miscibility with varied oils such as mineral, alkylbenzene and ester oil is tested. This test is performed by Mr. Andrew Swallow in Castrol Limited. Miscibility results of Castrol products (Icematic series) with THR02 are shown in Table 2.

Table 2 LCST (℃) of Icematic series of oils with THR02

% Oils in Gas	SW22 (Ester)	SW32 (Ester)	SW100 (Ester)	ZL150TD (AB)	ZL200TD (AB)	266 (MO)
5	<-60 (Hazy @ -45)	<-60 (Hazy @ -40)	<-60 (Hazy @ -42)	<-60 (Hazy @ -40)	<-60 (Hazy @ -50)	-58 (Hazy @ -35)
10	<-60 (Floc @ -35)	<-60 (Hazy @ -25)	<-60 (Hazy @ -21)	<-60 (Hazy @ -32)	<-60 (Hazy @ -20)	-45.5 (Hazy @ -20)
15	<-60 (Hazy @ -40)	<-60 (Hazy @ -10)	<-60 (Hazy @ -17)	<-60 (Hazy @ -16)	<-60 (Hazy @ -20)	-45.5 (Hazy @ -13)
20	<-60 (Hazy @ -30)	<-60 (Hazy @ -5)	<-60 (Hazy @ +7)	<-60 (Hazy @ -16)	<-60 (Hazy @ -15)	-45.5 (Hazy @ -7)
40	<-60	<-60 (Hazy @ -5)	<-60 (Hazy @ +7)	<-60 (Hazy @ -16)	<-60 (Hazy @ -13)	-14 (Hazy @ -6)

THR02 is a mixture of CF_3I , HFC and HC. All components were obtained commercially from chemical suppliers with a namely purity greater than 99.5% (water content ≤ 10ppm). But the sample were tested without analysis, further purify and drier. There appears to be some haze at the lower temperature end in all cases with this refrigerant. This was not floc at all, but a general haze, which was in all cases with the different lubricants. So we presume it is due to a high water content in the refrigerant. But we have no means of assessing the water content in refrigerant. Without this aspect, the results show that THR02 can be miscible with various lubricants in refrigeration applications.

MATERIAL COMPATIBILITY

THR02 is availed as foregoing. A commercially available mineral lubricant with a viscosity of 32 cst was used. Whole of refrigerants and oil were tested without further purified and dried. Compatibility tests were carried out at 120℃, 2.4MPa for 14 days. Results listed in Table 3~5.

Table3 Appearance Estimation for Sample / Oil After Test

Sample	R12		THR02	
	Oil	Sample	Oil	Sample
Cu	clear, no sediment	no change	clear, no sediment	white on the surface
Al	------	------	------	no change
PET	------	elastic, no fragile	------	elastic, no fragile
PBT	------	------	------	------
Enamel wire	------	no varnish drop after winding and twist	------	no varnish drop after winding and twist
Tie cord	------	soft, flexible	------	soft, flexible
Gasket	------	elastic, flexible	------	elastic, flexible
Plastic Pipe	------	soft, flexible	------	soft, flexible

Table 4 Weight Changes after Test

Sample	R12			THR02		
	before test (mg)	after test (mg)	change (%)	before test (mg)	after test (mg)	change (%)
Cu	176.37	176.40	+0.02	254.12	254.00	-0.05
Al	115.83	115.83	0.00	130.01	130.02	+0.01
PET	59.99	60.84	+1.42	60.74	62.34	+2.63
PBT	303.98	306.98	+0.99	270.89	275.96	+1.87
Enamel wire	18.42	18.45	+0.16	19.03	19.03	0.00
Tie cord	16.17	16.44	+1.67	15.88	16.27	+2.46
Gasket	31.04	31.58	+1.74	34.09	35.52	+4.19
Plastic Pipe	87.91	91.03	+3.55	81.01	83.42	+2.97

Table 5 Size Changes after Test

Sample	R12			THR02		
	before test (mm)	after test (mm)	change (%)	before test (mm)	after test (mm)	change (%)
Cu	7.043	7.047	+0.06	9.913	9.903	-0.10
Al	9.390	9.390	0.00	10.769	10.768	-0.01
PET	0.263	0.269	+2.28	0.267	0.270	+1.12
PBT	22.088	22.140	+0.24	21.731	21.853	+0.56
Enamel wire	0.492	0.491	-2.03	0.492	0.491	-2.03
Gasket	0.435	0.445	+2.30	0.435	0.445	+2.30

The changes for THR02 are slight larger than that for CFC-12, but they are basicly same and in the permissible range for use.

The material compobility test reached the same results with the accelerated compressor aging test. The parameters of compressor and lubricant have no change basically.

R/F TESTING RESULTS

A two-gate refrigerator BCD-181 was used for experiments. Based on without changing lubricants

and modifying the refrigerator, the mixture THR02 was used directly as "drop in" refrigerant instead of CFC-12. Tests were conducted on pull down, power consumption, the running time and the storage temperatures. The refrigerator has been running for two years, and the results are compared before and after two years running. As seen from table 6, the changes are very small.

Table 6 The comparison of the refrigerator performance before and after two year running

Item		1995.7	1996.7	1997.7
Pull Down (ambient temp.=32℃)	Freezing compartment (-18℃)	65 min	65min	67min
	Fresh food compartment (5℃)	105 min	110 min	117min
Energy Consumption (ambient temp.=25℃)	Freezing compartment (℃)	-18.0	-18.22	-18.13
	Fresh food compartment (℃)	4.74	4.60	4.71
	Running Time (%)	26.5	29.5	30.3
	EC (kWh/24h)	1.056	1.078	1.079
Storage Temperature (ambient temp.=32℃)	Freezing compartment (℃)	-19.9	-20.5	-19.7
	Fresh food compartment (℃)	3.45	3.43	4.19

COMPOSITION ANALYSIS AND PERFORMANCE CHANGE

A major concern shared by users about the mixture refrigerants is the potential for the mixture to change composition in a system. Using GC chromatograph, We measured the composition (both liquid and vapor phase) change when THR02 leaked out from a container at ambient temperature, the temperature fluctuation was within ± 0.5℃. Results are listed in Table 7~9. As seen in Table 9, at liquid leakage, composition changes are very samll and negligible. This is the reason that the mixture should be charge from the storage cylinder to the system as liquid in order to preserve the composition percentage.

Then we developed a computation model to simulate the other conditions as UL 2182 defined[4,5,6]. The computation results were contrasted with the tests shown in Fig. 2~4. The worst fraction case was at boiling tempurature +10℃, 15% full container, vapor leakage. The worst compositon is unflammable shown in Fig. 5.

Table 7 Composition change (vapor leakage, 18℃, 15% full)

Leak rate (%)	Vapor composition			Liquid composition		
	C	A	B	C	A	B
0.00	29.23	49.27	21.50	37.11	51.05	11.84
10.08	30.17	50.55	19.27	38.00	50.94	11.08
16.85	30.38	49.38	20.24	39.20	50.42	10.37
26.12	31.37	51.32	18.71	39.06	51.39	9.60
36.87	32.15	50.43	16.42	41.30	50.85	7.85
42.35	33.30	51.78	14.92	42.11	51.37	6.52
48.38	33.55	51.56	14.89	40.79	52.45	6.76
59.47	36.02	52.37	11.59	42.51	52.45	5.04
70.43	36.18	53.44	10.38	44.70	51.61	3.69
74.56	37.52	53.63	8.85	46.40	50.47	3.13
82.88	40.69	52.76	6.55	48.65	49.43	1.92
91.41	42.42	52.69	4.89			
98.04	44.18	51.34	4.47			

Table 8 Composition change (vapor leakage, 24.5℃, 90% full)

Leak rate (%)	Vapor composition			Liquid composition		
	A	B	C	A	B	C
0.00	51.62	17.59	30.78	53.60	9.74	36.66
6.20	51.73	17.45	30.74	52.34	9.26	38.40
14.30	52.23	17.04	30.73	52.55	8.60	38.85
18.26	54.34	13.57	32.09	53.33	8.06	38.61
23.87	53.23	15.20	31.55	53.16	7.12	39.73
38.43	54.26	12.91	32.82	52.74	5.62	41.64
44.98	54.45	12.04	33.51	53.14	4.69	42.17
53.31	53.74	9.87	36.23	53.26	3.71	43.03
74.12	56.51	4.03	39.46	51.94	1.38	46.67
83.65	53.34	2.56	44.10	51.70	0.73	47.57
90.76	54.27	1.07	44.66	48.83	0.21	50.96
98.31	47.21	0.08	52.71			

Table 9 Composition change (liquid leakage, 23℃, 90% full)

Leak rate (%)	Vapor composition			Liquid composition		
	A	B	C	A	B	C
0.00	51.57	15.58	32.85	53.35	8.09	38.56
1.07	50.13	15.83	34.05	53.62	8.06	38.32
5.92	52.60	15.66	31.75	53.32	7.90	38.78
12.55	51.72	15.46	32.82	53.44	7.91	38.65
23.29	51.27	16.10	32.63	53.21	7.90	38.89
31.53	51.73	15.92	32.35	53.83	8.35	37.87
41.61	51.73	16.66	31.61	53.69	8.14	38.17
46.04	51.65	16.01	32.34	53.79	7.98	38.24
62.25	52.19	15.98	31.83	53.64	7.99	38.27
68.05	52.23	15.69	32.08	53.66	8.05	38.29
73.37	52.07	15.91	32.02	53.36	7.96	38.68
78.84	52.33	15.81	31.85	53.33	7.91	38.76
89.83	52.06	15.84	32.10	53.22	7.85	38.93
94.31	52.25	15.76	31.98	53.31	7.93	38.77
98.83	51.56	15.64	32.80			

The charge-leak-recharge cycle was also simulated, the changes of composition and performance (without taking into account the change occured due to loss of charge weight) under refrigerator condition were listed in Table 10. The model calculation assumed that after 20% amount of leakage, the recharge would be made up using the original composition liquid, and this process repeated 5 times. The composition shown in Tab.10 is the composition difference with the normal composition. The original parameters are listed in column "0". Other data are the value after leakage.

As can be seen from table 10, the composition changes are very small. The performace parameters changes caused by the fraction are negligible. In applied system, the loss of capacity will only resulted from the loss weight of charge.

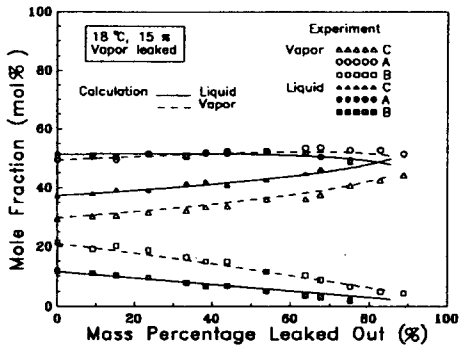

Fig.2 Calculation contrast with Tab.7 data

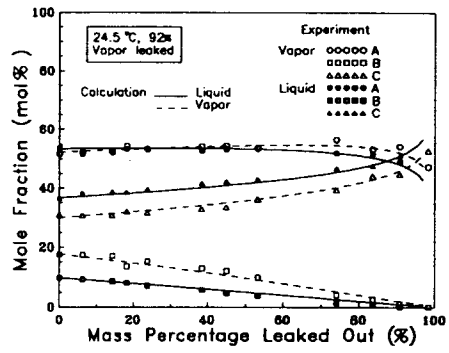

Fig.3 Calculation contrast with Tab.8 data

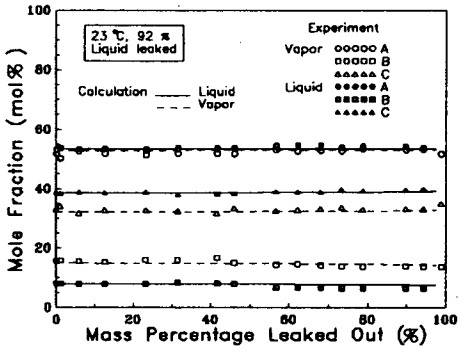

Fig.4 Calculation contrast with Tab.8 data

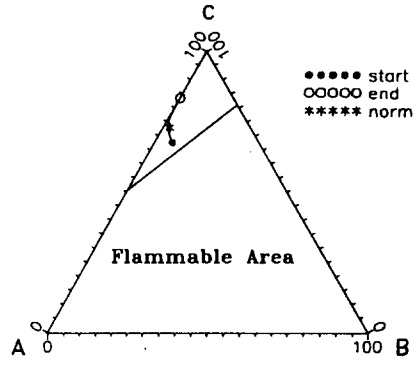

Fig.5 Unflammability of the worst case

Table 10. The parameter changes at leak-recharge cycle

Recharge		0	1	2	3	4	5
Vapor	CF_3I	-3.60	-3.57	-3.69	-3.78	-3.85	-3.91
	A	+1.66	+1.66	+1.70	+1.73	+1.75	+1.77
(wt %)	B	+1.93	+i.92	+1.99	+2.05	+2.10	+2.14
Liquid	CF_3I	+0.41	+0.43	+0.35	+0.28	+0.23	+0.19
	A	-0.19	-0.20	-0.16	-0.13	-0.10	-0.08
(wt %)	B	-0.22	-0.23	-0.19	-0.15	-0.13	-0.10
Pevap., bar		1.160	1.162	1.163	1.164	1.164	1.165
Pcond., bar		13.489	13.500	13.508	13.516	13.522	13.526
Pres. Ratio		11.628	11.623	11.619	11.616	11.613	11.611
Tdischarge, ℃		151.47	151.44	151.42	151.39	151.37	151.36
Glide	GTcond.	0.78	0.79	0.80	0.81	0.81	0.82
Temp., ℃	GTevap.	1.08	1.09	1.10	1.12	1.12	1.13
COP		1.0	.9999	.9998	.9997	.9997	.9997
Q0		1.0	1.0013	1.0024	1.0032	1.0039	1.0044
Qv		1.0	1.0010	1.0016	1.0023	1.0027	1.0031

CONCLUSIONS

THR02 is a promise refrigerant as a long-term alternative to CFC-12 and HFC-134a. The advantages are lists in follows:

1. Environment friendly. ODP=0, GWP≈50 (100yr. CO_2=1)
2. Safety. Nonflammable, no toxicity.
3. Near-Azeotropic. Glide temperatures of the evaporator and condenser are ≤1°C.
4. "Drop-In". Non modifying existing system, lubricant oil and compressor. Similar operating pressure and temperature to CFC-12 and HFC-134a.
5. Good thermal performance. The COP and q_v value are equal to or higher than CFC-12 or HFC-134a.
6. Reliability. THR02 is compitible with the former system materials. After the accelerated aging test, the compressor and lubricant have no change. Also, after two year running, the performance of the refrigerator has no change.

ACKNOWLEDGMENT

We are grateful to Mr. Andrew Swallow for carrying out the miscibility test with Icematic Oils at Castrol Limited.

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Selections and Applications of New Refrigerants for Air Conditioners

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New Refrigerants Applications Project
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1. Introduction

Today, the biggest challenge for the air conditioning industry is to provide safe and comfortable living while protecting the global environment. We have selected HFC refrigerants which contain fluorine but not chlorine as candidate alternative refrigerants. These candidates must not deplete ozone layers, must satisfy required characteristics such as performance and stability, and their safety must be verified in the market. We have narrowed down these candidates to a zeotropic refrigerant blend R-407C for applications to air-cooled packaged air conditioners and a high pressure refrigerant blend R-410A for application to split-type room air conditioners in Japan. This paper explains the reasons for selecting them and the technological developments which lead to successful application of these alternative refrigerants to air conditioners.

2. Transition of refrigerants

Fig.-1 shows the history of refrigerants used for air conditioners. The first change is the invention of the first non-toxic and non-flammable refrigerant, the fluorocarbon R-12 by Dr. Midgeley in the U.S.. The invention of this fluorine-based refrigerant brought forth an innovative change in the refrigeration and air conditioning market and was the driving force to expand the private air conditioning market.

The second change[1)] is the appearance of R-22 in the U.S.. A nontoxic and nonflammable refrigerant of higher pressure was produced by displacing a chlorine atom with a hydrogen atom. This enabled to miniaturization of equipment and higher efficiency. The appearance of R-22 further expanded the air conditioning market.

The third change is the fact that in 1974 Prof. Roland in the U.S. predicted that the chlorine content in fluorine-based refrigerants would deplete the ozone. Development of HFC refrigerants not containing chlorine and products applying these refrigerants started. Since 1992 the JAREP in Japan started its activities for evaluating the performance of candidate refrigerants[2)] for Room Air Conditioners (hereafter referred to as RA) and Air-cooled Packaged Air Conditioners (hereafter referred to as PA), cooperating with AREP..

3. Characteristics of Candidate Refrigerants

Table-1 shows the characteristics of the candidate refrigerants. Based on a concept that the highest priority must be put on safety, two mixed refrigerants R-407C and R-410A approved as nonflammable and nontoxic by the ASHRAE Standard are currently considered as candidate

alternatives.

4. Evaluation and Selection of Refrigerants

Two controversies exist for selecting refrigerants. One is "which refrigerant is economical and advantageous in performance?" and the other is "is it acceptable to put a zeotropic refrigerant into practical use?".

4-1 Comparison of Performance between R-407C and R-410A

Fig.-2 show COP under cooling operation of RA and PA. Since the volumetric capacity of R-407C is equivalent to that of R-22, a compressor's cylinder displacement of R-407C is equivalent to that of R-22. Since a volumetric capacity of R-410A is 1.4 times of that of R-22, the compressor displacement was decreased in proportion to this ratio. According to the compressor efficiency evaluation results, both the efficiencies of R-407C and R-410A are equivalent to those of R-22 within the tolerance of $\pm 1\%$. The new type heat transfer tubes are applied to heat exchangers of outdoor units and the refrigerant paths of heat exchangers are optimized taking the refrigerant characteristics into account. The tube thickness for R-410A units is increased to satisfy the requirements for high pressure.

The performance of R-410A heat pump RAs is better than that of R-407C RAs. On the other hand, both the performance of R-407C and R-410A of PAs are equivalent. Since R-407C is a zeotrope, counter flow type exchangers are effective for increasing capacity of heat exchangers. The test results show that COP of a straight R-407C cooling unit with counter flow type heat exchangers is 3% higher than that of heat pump.

Fig.-2 show that the effect of the new type heat transfer tube when used with R-407C is greater than that used with R-410A.

As presented by many reports[3)] on the heat transfer performance of zeotropic refrigerants, the heat transfer performance under both evaporation and condensation drops, because in addition to the temperature boundary layer a concentration layer is formed. Due to the advancement of manufacturing technology, a new grooved heat transfer tube was developed to take over the conventional spiral heat transfer tube and as a result, a heat transfer performance of almost two times of the conventional one is obtainable. The increment of COP is larger in R-407C than in R-410A, because the increase of heat transfer coefficient on refrigerant side cause a larger effect at low heat transfer coefficient than at high heat transfer coefficient. Another test result show that the COP of R-407C can be improved by the use of liquid to liquid heat exchanger for subcooling[4)].

In the past when refrigerants changed from the low pressure R-12 to the high pressure R-22, this change was the catalyst for miniaturization of equipment and popularize heat pumps and split systems. Some people view, therefore, that the change from R-22 to the high pressure R-410A may contribute to further miniaturization and cost reduction of equipment. This paper refers to this point from the standpoint of refrigerant evaluation for air conditioning equipment.

Fig.-3 shows the comparison of effect between the change from R-12 to R-22 and that from R-22 to R-410A. The former change improves the volumetric capacity by 60% without reducing the theoretical COP within the whole range of practical condensing temperature (40 to 70 degC). Since the volumetric capacity increment results in reduction of refrigerant pressure loss and as a consequence, the evaporating temperature rises. Thus the change from R-12 to R-22 greatly contributed to the improvement of the performance and the miniaturization of equipment. On the other hand, though the latter change brings forth the effect equivalent to that of the former within the condensing temperature range below 30 degC, as the condensing temperature rises, the increment of volumetric capacity decreases and the COP remarkably drops. This difference is derived from the difference of the critical temperature of R-22 and R-410A. In general, the condensing temperature of air cooled equipment is around 45 to 50 degC under rated conditions and in this range both the volumetric capacity and the theoretical COP greatly differ from those of the change resulting from R-12 to R-22.

Fig.-4 shows a comparison of PA performance under the condition of cooling overload (when the outdoor temperature is high) between R-407C and R-410A. As the outdoor temperature rises, the capacity of R-410A equipment remarkably drops and the COP decreases. In comparison with RAs, PAs are more often installed in a narrow spaces between buildings and shops or operated under severe conditions in Japan. However, they are expected to give sufficient cooling performance even if they are operated under these conditions. From this point of view, R-410A equipment of low critical temperature is still a serious problem that needs to be solved.

Fortunately the refrigerant pressure loss of R-410A is lower than that of R-22 and this advantage is effective when the refrigerant pressure loss is relatively high in an evaporator and low pressure side piping. Fig.-5 explains this state.

Depending on the heat exchanger design concept, this effect may become obvious. In case of inverter controlled RA, in order to heat up a room in a short time, it is required to increased the capacity ratio of heating to cooling. For this reason, when designing indoor heat exchangers the priority is given to obtain larger heating (condensing) capacity. Therefore, for the purpose of condensation, it is beneficial from the capacity point of view to design a heat exchanger with fewer paths and increase refrigerant mass flux. However, when used as an evaporator under cooling operation, the refrigerant pressure loss of the medium pressure refrigerants such as R-22 becomes large (0.06 to 0.08 Mpa with R-22 equipment) and causes a reduction in evaporating capacity. Therefore, if the lower pressure loss refrigerant R-410A used, it is possible to design a path to maintain condensing capacity under heating operation without reducing evaporating capacity under cooling operation. The cooling COP, therefore, can be maintained relatively high. In general, PAs are designed to output almost the same capacities of heating and cooling, and the priority is given to cooling operation when designing heat exchangers. Since the evaporating pressure loss which

causes lower evaporating capacity is designed to be minimum even for R-22 equipment, the effect obtained by using R-410A is small.

When putting R-410A into PAs, the material cost of pipes, pressure vessels and components increase due to the increase in pressure. For the moment of performance corresponding to the cost increase cannot be obtained unless the refrigerant pressure loss is extremely high. The capacities of RAs are relatively small size copper tubes such as 1/4" and 3/8" are mostly used. Due to the problems inherent in the manufacture of extremely small copper tubes, the thickness of these tubes are determined by the JIS. Tube for use with R-22 are lager than the required thickness for R-410A pressure tubes. Therefore, the material cost increases due to thickness is small. In Japan, RAs equipped with inverters are popular, since it enable higher heating capacity. As shown in Fig.-2 the performance of R-410A is superior to R-407C in case of RA with higher capacity in heating than in cooling. Therefore, R-410A is selected.

On the other hand, due to technological development of heat transfer tubes, the performance of R-407C PAs equivalent to R-22 can be obtained. Since the pressure of R-407C is nearly equivalent to that of R-22, the increase in material costs is small. In addition, the overload performance of R-407C under cooling operation is fairly good. Therefore, R-407C was selected as the alternative refrigerant for PAs.

Currently both R-407C and R-410A still have problems to be solved in comparison with the superior refrigerant R-22. It is necessary to use these refrigerants properly taking characteristics in account.

4-2 Evaluation of Practicality of Zeotropic Refrigerants

Fig.-6 and Fig.-7 show the evaluated results of practicality of an azeotropic refrigerant. Fig.-6 shows the capacity change after the gas rich in low boiling point component leaks and then the normal composition liquid is charged again. The capacity drop is at worst 5%. Even in the case of a single component refrigerant, the capacity change is inevitable, because there is no way to measure accurately the amount leaked for additional change. As a consequence, the additional change amount is more or less out of the normal range. As a rule of thumb, if the refrigerant is short by 20%, the capacity also drops by approximately 20%. Therefore, this 5% drop in capacity due to zeotropic refrigerant can be ignored for all practical purposes.

Fig.-7 shows the composition change of a charged refrigerant when it is charged from a service cylinder. The configuration of a cylinder is shown in the figure. Unlike conventional single component refrigerants it is necessary to charge the refrigerant in the liquid state. For that reason a dip tube is inserted into the cylinder so that the refrigerant can always be charged in the liquid state. If the liquid refrigerant in the cylinder becomes small, the gas weight in comparison with the liquid weight cannot be ignored and the comparison of the charged liquid refrigerant gradually shift to one with high boiling point characteristics. Even after all liquid is charged, the influence on

capacity is small and is within ±1% of the rated capacity. If the composition at the initial charge is shifted beforehand to the low boiling point side, the capacity drop can be lessened. As for this point the zeotropic refrigerant has no practical problems.

Even in a complicated system such as VRV(Valuable Refrigerant Volume System), the test results show that an abnormal composition shift does not occur under various operation modes. For instance, even if the refrigerant accumulates in the indoor unit not operating in heating mode, the accumulated liquid refrigerant is in the subcool region and its composition becomes similar to the circulating gas. Therefore, the composition balance is maintained. The test results also show that the composition dispersion of two phase refrigerant after a branch to each indoor unit is small.

The other test results show that the composition shift under non-steady or the protection device actuation after gas leakage did not cause the problems we first worried about.

According to the investigation of problems likely to be caused by zeotropic characteristics, we conclude that the zeotropic refrigerant R-407C can be put into practical use.

5. Tasks and Examples of Technology Development

As shown in Fig.-1, HFC refrigerants do not contain chlorine atoms. The chlorine atom contained in HFC refrigerants forms iron chloride after reacting with on the sliding surface of compressors and the iron chloride film results in lubricating effect. Therefore, the compressor sliding surface drops with the HFC refrigerants with do not contain chlorine atoms. Therefore, it is necessary to redesign lubrication system (i.e. change of bearing materials). In addition, it is necessary for R-410A to redesign bearings for high pressure use.

The HFC refrigerants which do not contain chlorine have strong polarity. The conventional mineral oils used with R-22 do not have polarity and are not soluble in HFC refrigerants. Therefore, synthetic oil that is soluble in HFC refrigerants or has polarity is required in lieu of mineral oil. Refrigerating machine oil is a key component for refrigeration machines and it is essential to verify its reliability[6].

Supplementary materials used during manufacturing processes such as machining, rust prevention and cleaning remain in a refrigeration cycle as contamination. Most of contamination are non-polarity substances. In addition, if the sliding parts of a compressor come in contact with metals, a phenomenon of localized high temperature occurs and highly reactive impurities and extreme-pressure additives originally contained in oil react and sticky sludge is produced. This sludge is a substance without polarity. Since substances without polarity are not soluble in HFC refrigerant with polarity, these substances with polarity deposit in the liquid refrigerant. These deposits adhere to narrow parts such as capillary tubes, expansion valves and needle valves, and cause clogging. As a result, these may cause compressor breakdown due to high compressor discharge temperature or malfunction of expansion valves. Therefore, it is necessary to take effective measure in order to prevent them.

Fig.-8 is a rough illustration of the compressors used for RA. Since the tip of the rotary compressor vane shown on the right forms line contact with the roller periphery, the contact face is large and a metal contact is formed. Sludge is produced on this sliding face and causes capillary clogging. On the other hand, the sliding surface of the swing compressor which we have newly developed is not so severe, and as a result, it does not produce sludge.

There are reports on prevention of clogging by applying new materials to vanes and rollers[7].

We evaluated compressor types and kinds of oils from the view point of capillary tube clogging and oil deterioration. Table-2 shows the characteristics of ester oil (POE) and ether oil (PVE) , the major candidate oils.

Fig.-9 shows the test results of RA. The material suitable for HFC is used in the rotary compressor vanes. The total acid numbers which express the oil deterioration degree show no difference between these oils. The test results show that our swing compressor is superior to our rotary compressor and ether oil is superior to ester oil. The reason the type is superior is because sludge is not produced on the sliding surface. The reason why ether oil is superior is because solubility of contaminants in ether oil is higher than that of ester oil. One more reason is because the amount of extreme pressure additive which becomes a cause of sludge is less in ether oil than in ester oil[8].

Fig.-10 show the test results of PA. A scroll compressor is mounted and an electronic valve is used in lieu of a capillary tube. The problem with ether oil is that it easily becomes oxidized and deteriorates. For evaluation purposes, air was forced into the refrigerant system after the system was evacuated. The predictable maximum air volume during installation was forced into the systems. The test results show that clogging of the electronic expansion valve by ether oil is less than that of ester oil under continuous and when not is operation[9].

The above test results show that ether oil has better compatibility characteristics when used with a swing compressor mounted on a RA with a capillary tube. The results also show that ether oil is beneficial with a scroll compressor and electronic expansion valve mounted PA.

6. Future Direction

Today we are confronted with a new issue of global warming prevention. For prevention of global warming, it is necessary to establish a system to recover and destroy refrigerants to prevent refrigerant release into the atmosphere. The industry is currently on the move to establish an effective system.

Investigation on refrigerants which hardly affect global warming is currently proceeding as well as prevention of releasing refrigerants into the atmosphere. This paper in the previous chapters discusses nonflammable refrigerants, of which safety can be verified. If the number of fluorine atoms is increased in a refrigerant molecule for non-flammability, the life of the refrigerant in the atmosphere becomes long and the global warming potential increases. In addition, if the number of

hydrogen atom is increased, the global warming potential decreases and the volumetric capacity increases without the remarkable drop in COP[10),11),12)]. Therefore, the direct and indirect global warming effect can be reduced, and the flammability of the refrigerant increases. That is, when we took into the characteristics of refrigerant, we know that prevention of global warming theoretically conflicts with control of flammability.

In order to make the functions of safety, comfort and prevention of global warming coexist, the key depends on balancing the numbers of H-atom and F-atom which have conflicting properties. F-atoms play an indispensable role in optimizing this balance. In this sense, for the technical solution on global warming, it is most important to clarify the evaluation results of safety on refrigerant[13),14)].

Today engineers must use their knowledge to solve two significant problems. One is to improve efficiency of air conditioning equipment using nonflammable refrigerants and establish a recovery system. The other is evaluation of the safety of flammable refrigerants which greatly contribute to the reduction of the global warming effect.

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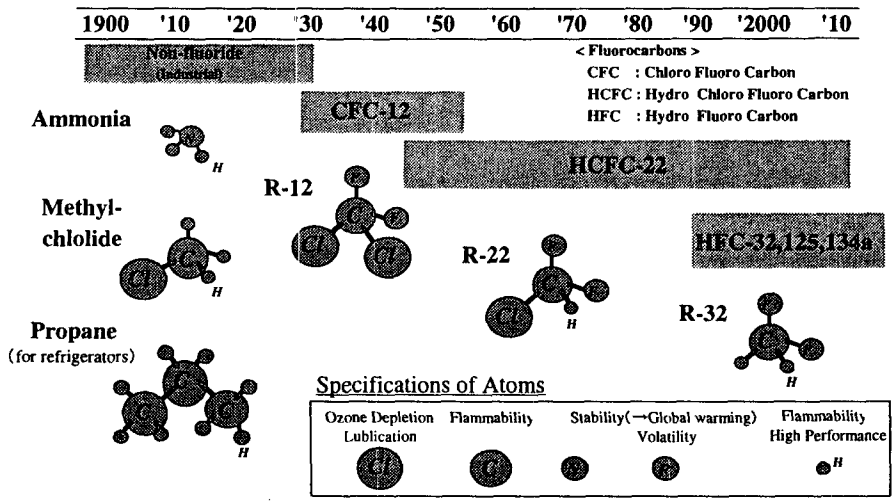

Fig.-1 History of Refrigerants for Air-Conditioners

Table-1 Specifications of Alternatives for HCFC-22

Refrigerants			Properties						
			Critical T ℃	High Press. kg/cm2 *3	ODP *4	GWP *5	Capacity	COP	Heat Transfer
	HCFC-22	Pure	96	18.8	0.05	0.43	100	100	○
Alternatives	HFC-134a	Pure	101	12.4	0	0.33	62	98	○
Alternatives	HFC-407C *1)	Non-azeo.	86	20.5	0	0.38	98	95	△
Alternatives	HFC-410A *2)	Near-azeo	73	30.2	0	0.43	140	89	○
Alternatives	HFC-32/134a (30/70wt%)	Non-azeo.	94	19.1	0	0.28	96	99.5	△
Alternatives	HFC-32	Pure	78	31.0	0	0.16	162	95	◎
Reference	HFC-125	Pure	66	24.8	0	0.70	86	73	△
Reference	Propane	Pure	97	16.4	0	0	82	95	○
Reference	Ammonia	Pure	132	19.7	0	0	118	107	◎

*1 HFC-407C=HFC-32/125/134a (23/25/52wt%)
*2 HFC-410A=HFC-32/125 (50/50wt%)
*3 Condensation Temp. 50℃
*4 ODP : Ozone Depletion Potential
*5 GWP : Global Warming Potential based Afeas 1995, relative to CFC-11, 100years

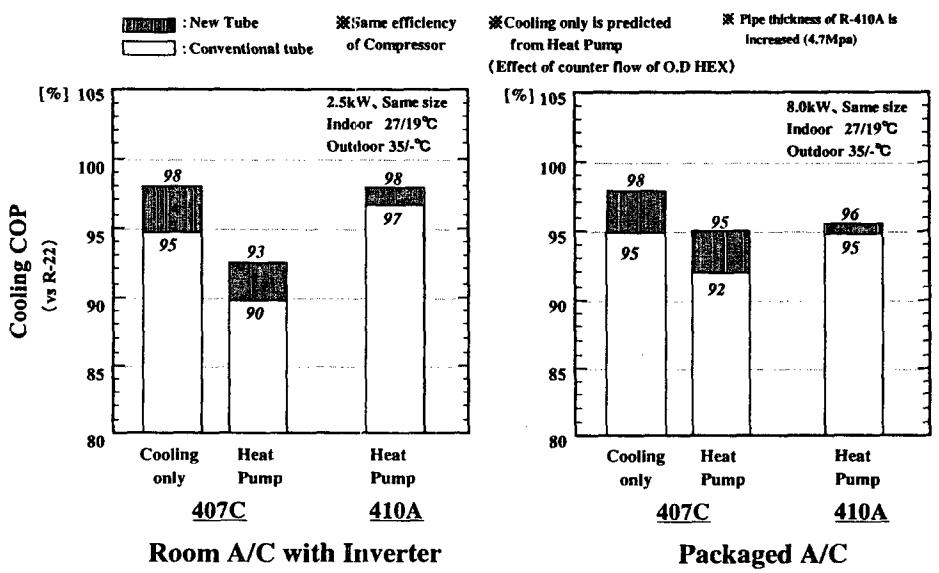

Fig.-2 Performance in Standard Condition

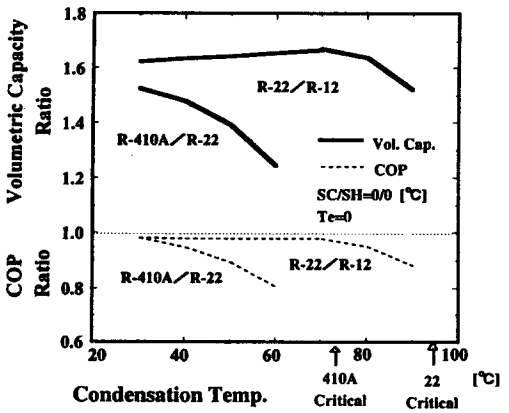

Fig.-3 Effects of High Pressurization

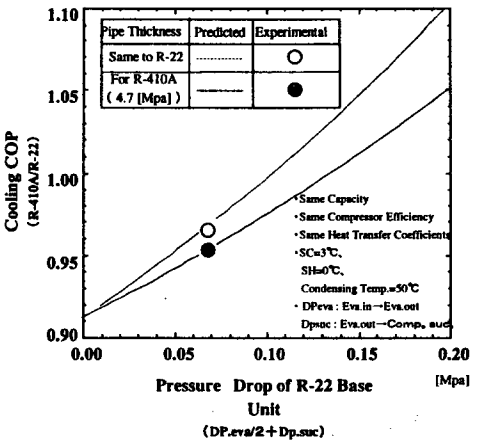

Fig.-5 R-410A COP and Low-side Pressure Drop

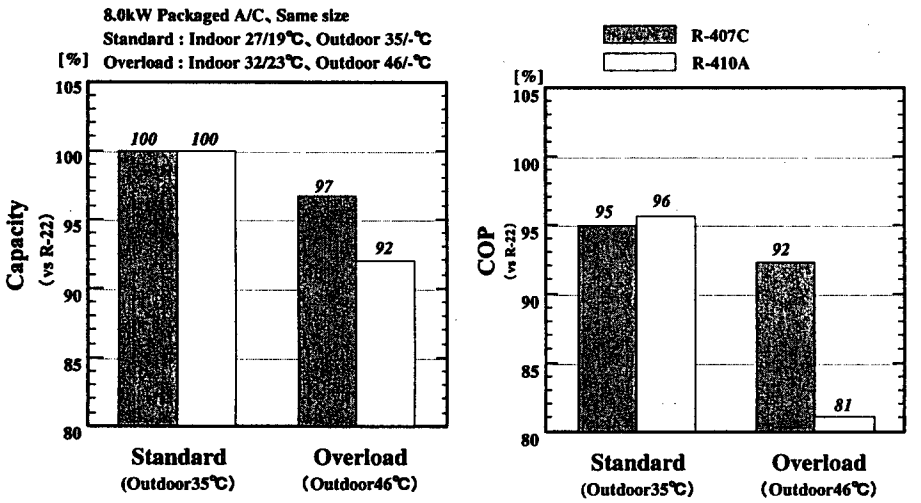

Fig.-4 Performance in Overload Cooling Condition

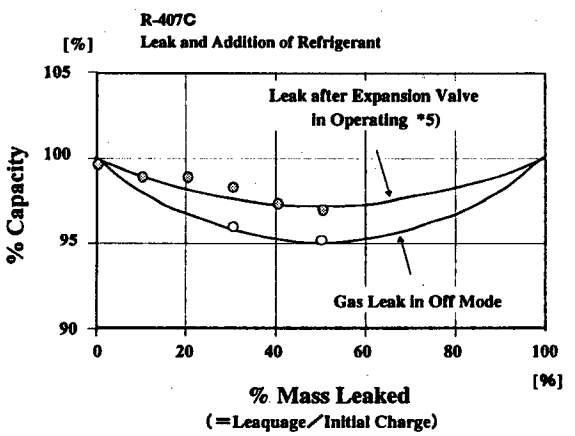

Fig.-6 Effects of Ref. Leak and Addition on Capacity

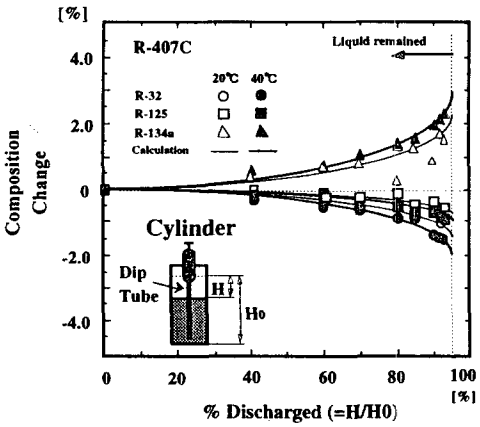

Fig.-7 Composition Changes during Liquid Charge

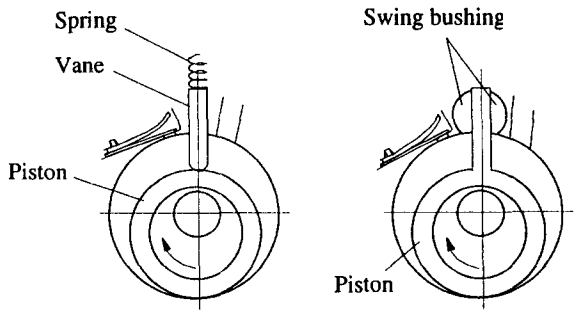

Fig.-8 Structures of Compressors for RAs

Table-2 Characteristics of Oils

	Ester (Polyolester)	Ether (Polyvinylether)	Mineral
Structure	R-COO-R	R-O-R	
Polarity	Yes	Yes	None
Solubility with HFC	◎	◎	×
Solubility with Non-polar Process Oil	×	△	○
Thermal Stability	○	○	○
Hydroysis	△	○	○
Oxidization	○	△	○

◎ : Better ○ : Good (equivalent to R-22/Mineral Oil)
△ : Worse × : Worst

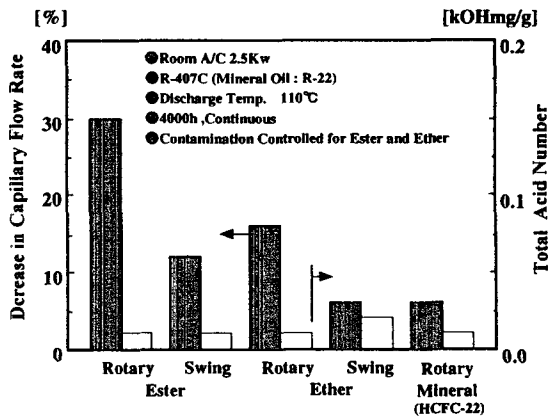

Fig.-9 Evaluation of Capillary Clogging

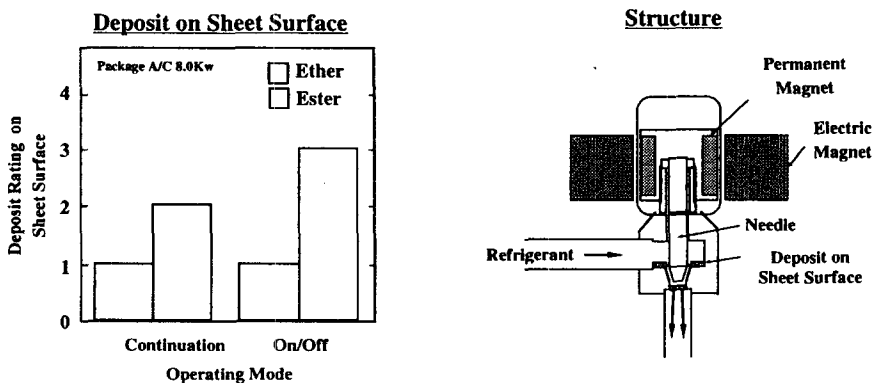

Fig.-10 Deposit Rating on Electric Expansion Valve (8.0Kw PA with Scroll Compressor)

EVALUATION OF FIRST-12 IN REPLACING CFC-12 IN REFRIGERATOR/FREEZERS

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Abstract:

This article introduces a new binary mixture refrigerant developed by Hangzhou First Chemical Co.Ltd. Composed of HCFC-22 and HFC-152a,which has a very low ODP (0.03) and GWP (0.3) value, it can be directly used to replace CFC-12 in the application of refrigerators and freezers. The article compares the substitute with CFC-12 and emphasizes its advantages.

Introduction:

Although CFC-12 has very good thermo-characteristics, owing to its depleting effect to the Ozone Layer,it is stipulated by Montreal Protocol as a substance which will be restricted in application and finally be phased out.

First-12 (HCFC-22/HFC-152a) is a near-azeotropic binary mixture substance. It has lower ODP and GWP. Pure HCFC-22 and HFC-152a have very good thermo-performances.If we use First-12 to substitute CFC-12,we do not need to change the main parts and process equipment of the refrigerators and chillers. So it is very convenient to transfer the system from CFC-12 to First-12. Also the energy consumption of First-12 is 5 --10% less than that of CFC-12. At the same time the cooling velocity of refrigerators and chillers is improved. Owing to the near-azeotropic characteristics,the concentration difference of the two substances in gas phase and liquid phase areas is small. There cause little influence to the cooling performance even if there is small leakage in the systems.

I. Temperature-concentration curves of First-12 refrigerant:

See Figure 1: Gas-Liquid equilibrium of First-12.

II. Thermo-dynamic performance of First-12 refrigerant:

See Figure 2: Thermo-dynamic performance of First-12.
Figure 2 shows the result of COP value, energy consumption W, cooling amount Qo, volume cooling amount Qv, compressor outlet tenperature T2, evaporate pressure Pe, cooling parts pressure Pc, and compressor pressure π ,when using the mixture in different mol concentration. The data showed in Figure 2 is the rate of First-12 with CFC-12.

The figure 2 tells that when the concentration of one component increases the Qv will increase but COP, Qo and W will decrease. When the concentration of one component is not more than 70%,the COP of the mixture is higher than that of CFC-12.

III. Saturated steam pressure curve and flammability test figures of First-12:

See Figure 3: Saturated Steam Pressure Curve of First-12
and Figure 4: Flammability Result of First-12.

IV. Recycling performance of First-12 in refrigerators and chillers:

Item / Characteristics	Cooling Temp.(°C)	Cooling Pressure (MPa)	Density (Kg/M3)	Enthalpy (KJ/Kg)	Entropy (KJ/Kg.K)
Low pressure saturated steam	-22.31	0.1199	0.004112	487.95	2.1517
Compressor inlet steam	32.00	0.1199	0.003334	538.25	2.3329
Compressor outlet steam	144.41	1.4509	0.03255	639.65	2.3329
High pressure saturated steam	55.50	1.4509	0.04615	540.36	2.0633
High pressure saturated liquid	54.60	1.4509	0.7686	308.67	1.3574
Streaming inlet	31.60	1.4509	0.8258	261.82	1.2093
Low pressure saturated liquid	-23.90	0.1199	0.9332	188.71	0.9555

V.Advantages of First-12.

1. It has lower ODP (<0.03) and GWP (0.3).
2. It has similar steam curve of CFC-12, the thermo-dynamic performance is similar to that of CFC-12.
3. It can save 5--10% energy than CFC-12.
4. It can be filled into the systems instantly. The main parts of refrigerators and chillers

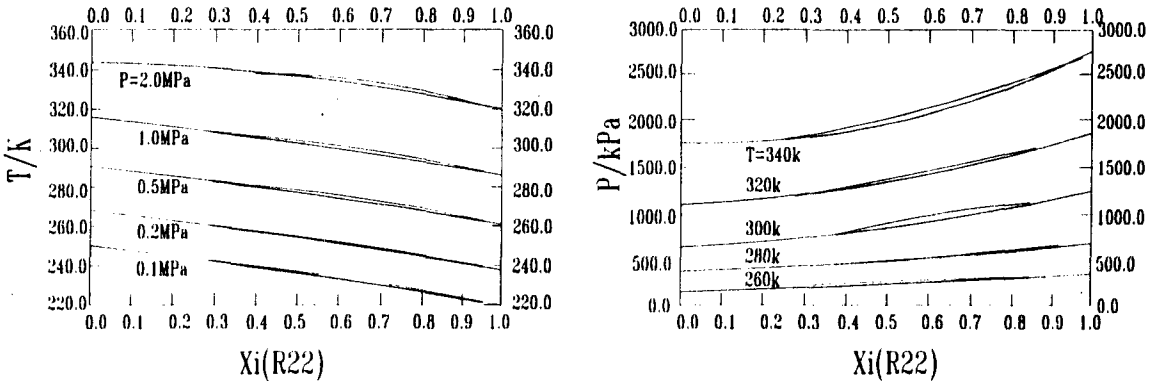
(compressors,coolers,evaporators,etc.) do not need reforming. It is very easy to transfer from the old manufacturing process to the the new green refrigerators. It is an interim route that meets China condition.

VI. Specifications in application of First-12.

1. When applying the refrigerant the old CFC-12 sealing facility and leak test equipment can be used. The process workshop should be installed with ventilation's system (using detonation-prevent fan,for example) and automatic alarm system.
2. For the compressor oil the mineral oil can be used. But it is better to use ester oil series.
3. For the drying materials XH-6 is most appropriate.
4. The filling amount can be reduced 20--30% comparing with CFC-12 system. The length of tube will be 0.3--0.8M longer than the old system.

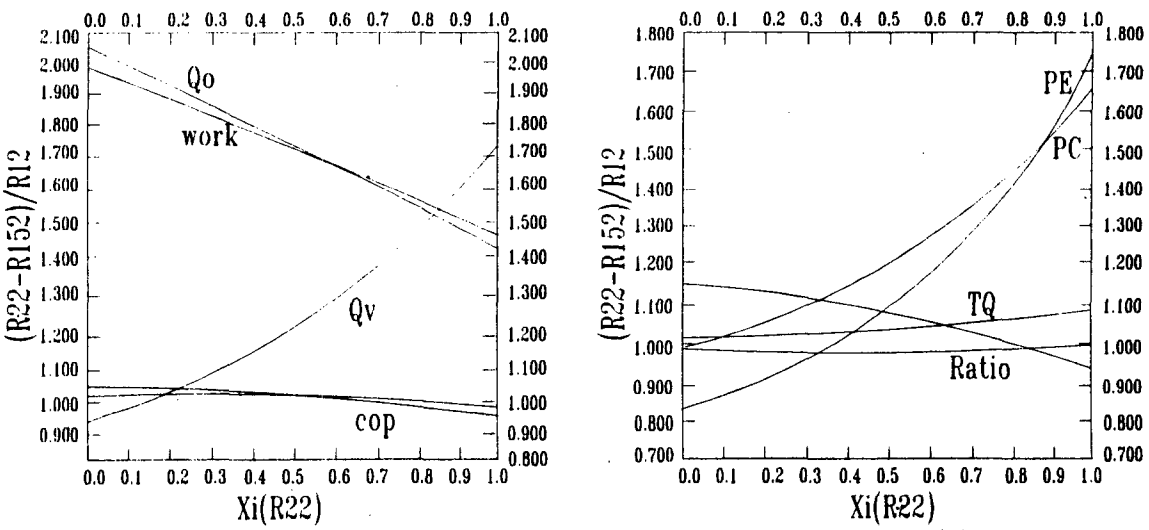
VII. References:

(Omitted)



(a) (b)

Figure-1:Gas-Liquid Equilibrium of First 12



(a) (b)

Figure-2:Thermo-dynamic Performance of First 12

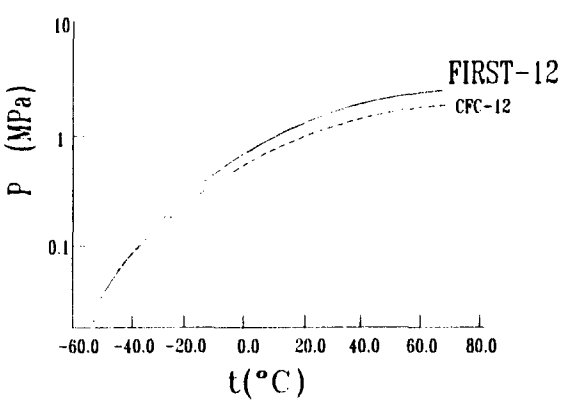


Figure-3:Saturated Steam Pressure Curve of First 12

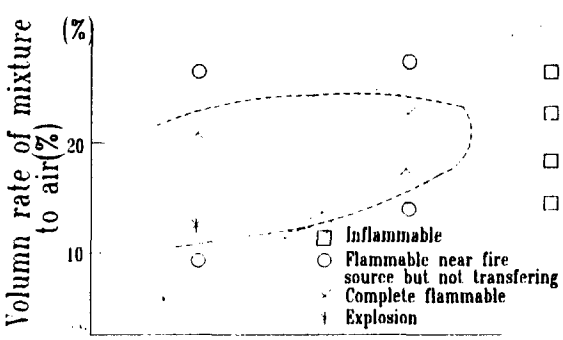


Figure-4:Flamability Result of First 12

Viscosity Modeling of Refrigerant/Lubricant Mixtures

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ABSTRACT

Under conditions of hydrodynamic and elastohydrodynamic loading, viscosity is the most important factor to consider in choosing a lubricant. Since the viscosities of refrigerants are much lower than those of lubricants, a small quantity of refrigerant dissolved in a lubricant can cause a significant reduction in mixture viscosity. In contrast to gas phase mixtures, where kinetic theory leads to reliable predictions of mixture viscosity, the theory for predicting the viscosity of liquid mixtures is not well developed. Several liquid mixture models have been proposed that partially account for both molecular size and differences in the Gibbs energy of activation between like and unlike molecular interactions. Most of these models have been implemented, in a practical sense, to include only binary interactions. They are also often unreliable in either the refrigerant rich or lubricant rich mixtures regions. In an attempt to correct for these deficiencies, a model similar to the Wohl [n]-suffix expansion for non-ideal liquid mixtures has been developed. In this model, n-body interactions are treated in a systematic manner. In addition, a non-linear composition scale, based on Wohl q-fractions, is introduced to more accurately represent molecular size differences between refrigerant and lubricant molecules. Comparisons of this model with several other viscosity models for mixtures, such as those proposed by Kendall, Grunberg-Nissan, and Yokozeki, have been made and applications to several refrigerant/lubricant mixtures are in progress.

Introduction

The introduction of new refrigerant/lubricant combinations for HVAC systems has brought about a need for developing reliable models to describe the viscosity characteristics of these new mixtures. Models based on empirical polynomial expansions in temperature and composition have often been used to describe mixture behavior. Almost all models assume or require that values of the viscosities of the pure components are known. Thus the primary feature for judging the validity of these models is their utility in interpolating data from the extreme limits of pure refrigerant and pure lubricant. It is well known that the viscosity of liquid mixtures is not a simple function of composition. Mixture viscosity may exhibit a maximum, a minimum or both over a specified composition range. For the pure components, the extended Andrade equation[1], a polynomial in temperature, is often used to represent viscosity. Studies show that a four or five term expansion can accurately represent viscosity over the normal operating range of interest, -20 °C to 80 °C, for both refrigerant and lubricant. The difficulties arise in developing reliable models to cover mixtures ranging from pure lubricant to high refrigerant dilution levels. Owing

to the large size differences between refrigerant and lubricant molecules, a reliable model must account for both the difference in molar volumes of refrigerants and lubricants and for differences in molecular interaction strengths.

Previous studies of the viscosity of liquid mixtures have focussed mainly on molecular systems of nearly equal size and have been mainly restricted to near-ideal mixtures. An ideal mixture is one that undergoes zero volume change and zero heat exchange upon mixing. For such mixtures, Arrhenius[2] proposed that mixture viscosity should be an additive property, linearly connected to the viscosity of the pure components. Mixtures which exhibit this type of behavior are typically non-polar. Examples are hydrocarbons and halogenated hydrocarbons, such as CFCs. The introduction of HFCs as refrigerants, which are much more polar, has led to the use of polar polyolester lubricants to improve solution solubility and miscibility. However, these new refrigerant/lubricant mixtures exhibit non-ideal character and very large molecular size differences between refrigerant and lubricant. In this paper, we examine several models for describing non-ideal solutions and describe a generalized model that can systematically address the physics of their non-ideal character.

Mathematical Models

An extensive review of empirical equations that have been proposed to describe the viscosity of binary liquid mixtures is presented in a technical report by Irving.[3] In this review, 318 binary mixtures covering a wide selection of liquids were tested against 25 mixture equations. Irving classified these equations into six different categories depending on their parametric dependence. Since we are interested in developing a model for a general multicomponent refrigerant/lubricant mixture, the first category, which Irving classified as additive equations, is examined. In this category, the viscosity of a mixture is represented formally as follows:

$$f(\eta_{mixture}) = \sum_i \phi_i f(\eta_i) \tag{1}$$

Here $f(\eta_i)$ is a function of the viscosity of pure component i, and ϕ_i is a metric for measurement of the composition of component i. If ϕ_i is taken as the volume fraction of component i and $f(\eta_i)$ is taken as $\ln \eta_i$, we have for a binary system:

$$\ln \eta_{mixture} = \phi_1 \ln \eta_1 + \phi_2 \ln \eta_2 \tag{2}$$

Equation (2) is commonly referred to as the Arrhenius equation[2] for ideal binary mixtures. It is useful for mixtures where there are no strong intermolecular forces (non-polar) and where there is no volume change upon mixing. A variation of equation (2) was proposed by Kendall[4] where composition is measured using mole fraction instead of volume fraction. Mixture equations of the additive type have been extended by adding terms with one or more disposable constants. An example is the Grunberg-Nissan equation[5], which for binary mixtures can be written as:

$$\ln \eta_{mixture} = \phi_1 \ln \eta_1 + \phi_2 \ln \eta_2 + 2\phi_1\phi_2 G_{12} \tag{3}$$

For binary polar mixtures, Irving[3] finds that the Grunberg-Nissan equation has the smallest average error when tested with nearly 1000 data points, taking ϕ_i as the mole fraction of component i and optimizing the value for the adjustable parameter, G_{12}, from mixture data. A variation of equation (3), based on a kinetic model involving binary pair activation energies, is due to Frenkel[6]:

$$\ln \eta_{mixture} = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1x_2 \ln \eta_{12} \tag{4}$$

In equation (4), x_i refers to the mole fraction of component i, and $\ln \eta_{12}$ is an interaction parameter between unlike molecules, usually determined experimentally from mixture data. Irving[3] finds that equations (3) and (4) have comparable accuracy, comparing both polar and non-polar mixtures.

Recently, Yokozeki[7] has proposed a viscosity mixture model of the type represented by equation (1):

$$\ln \eta_{mixture} = \sum_i \xi_i \ln \eta_i ; \quad \xi_i = \frac{m_i^k x_i}{\sum_j m_j^k x_j} \tag{5}$$

In equation (5), x_i and m_i refer to the mole fraction and molecular weight of component i respectively, and k is an empirical parameter, often modeled as a simple polynomial in the temperature. Yokozeki finds that $k \sim 0.58$ for many refrigerant mixtures but that k must be treated as an adjustable parameter for refrigerant/lubricant mixtures. For k=0, the Yokozeki model reduces to the model proposed by Kendall[4]. For k=1, the concentration measure becomes weight fraction rather than mole fraction. The Yokozeki model can be recast into the formalism first introduced by Wohl for describing non-ideal solution behavior.[8] Letting:

$$\xi_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{6}$$

where q_i is defined by Wohl as the effective collision volume of component i, we find :

$$\left(\frac{m_j}{m_i}\right)^k = \left(\frac{q_j}{q_i}\right) \tag{7}$$

the q-ratio familiar in UNIQUAC[9] and other solution theory models.

All of the models for viscosity of mixtures described above either neglect the effects of molecular interaction or attempt to treat those effects empirically. Some years ago, Eyring[10] proposed a model for the viscosity of liquids based on molecular theory. In this model, the shear between two molecular layers of liquid is represented as the passage of molecules from one equilibrium position to another by filling or creating a hole site in the liquid layer. The movement of a molecule into or out of this hole site is regarded kinetically as the passage of

molecules of the system over a potential energy barrier related to the Gibbs activation energy for the molecular interaction, ΔG^*. The relationship of the viscosity (shear stress/shear rate) to this activation energy can be written as:

$$\eta = \frac{hN}{V}\exp[\Delta G^*/RT] \tag{8}$$

where h is Planck's constant, N is Avogadro's number, and V is the molecular volume. ΔG^* represents the change in the Gibbs energy required for passage over an energy barrier. Eyring[10] has compared equation (8) against the viscosity of several types of systems, including long chain hydrocarbons and finds that ΔG^* can be represented approximately as $\Delta U/2.45$, where ΔU is the molar energy of vaporization. These studies suggest that ΔG^* should exhibit thermodynamic property behavior. For mixtures, the Gibbs energy, ΔG^*, can be written as an extensive thermodynamic property of the first degree in mole number:

$$\Delta G^*_{mixture} = \sum_i x_i \Delta G^*_i + \Delta G^{XS} \tag{9}$$

where the first term is the form for an ideal mixture and the second term arises from interactions between different molecular components in the mixture. Substituting equation (9) into equation (8) yields:

$$\eta_{mixture} = \frac{hN}{V}\exp\left[\left(\sum_i x_i \Delta G^*_i + \Delta G^{XS}\right)\Big/RT\right] \tag{10}$$

ΔG^{XS} represents the excess Gibbs energy of mixing and is small for mixtures of like molecules. Setting $\Delta G^{XS}=0$, for binary systems with $V_1 \approx V_2$, Eyring has shown[10] that equations (10) and (8) can be combined to yield:

$$\ln \eta_{mixture} = x_1 \ln \eta_1 + x_2 \ln \eta_2, \tag{11}$$

an expression identical to that proposed by Kendall.[4]

A different interpretation of ΔG^* has been proposed by McAllister[11] who expands ΔG^* in terms of 3- and 4-body interactions, with weighting equal to the identity of the collisional partners. Thus for 3-body collisions, we have the following terms for a binary system:

1	1	1	2	2	2	1	2
1	2	1	1	1	2	2	2
1	1	2	1	2	1	2	2
(a)	**(b)**	**(c)**	**(d)**	**(e)**	**(f)**	**(g)**	**(h)**

McAllister further assumes collisions of type (**b**), (**c**) and (**d**) are similar, as well as (**e**), (**f**) and (**g**). The energy of activation is then written as:

$$\Delta G^*_{mixture} = x_1^3 \Delta G_1^* + 3x_1^2 x_2 \Delta G_{12}^* + 3x_1 x_2^2 \Delta G_{21}^* + x_2^3 \Delta G_2^* \tag{12}$$

This expression for ΔG^* is substituted into equation (8), and after further approximation for the mixture volume and some algebraic manipulation, McAllister proposes the following equation for the kinematic viscosity of binary mixtures:

$$\begin{aligned} \ln \nu_{mixture} &= x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln\left[x_1 + \frac{m_2}{m_1} x_2\right] \\ &+ 3x_1^2 x_2 \ln\left[\left(2 + \frac{m_2}{m_1}\right)\Big/3\right] + 3x_1 x_2^2 \ln\left[\left(1 + 2\frac{m_2}{m_1}\right)\Big/3\right] + x_2^3 \ln\left(\frac{m_2}{m_1}\right) \end{aligned} \tag{13}$$

The factors $\ln \nu_{12}$ and $\ln \nu_{21}$ are treated as undetermined constants and equation (13) has sufficient flexibility to fit viscosity data for mixtures that exhibit both a maximum and a minimum as a function of composition.

Using similar arguments for 4-body collisions, McAllister finds:

$$\begin{aligned} \ln \nu_{mixture} &= x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} \\ &+ x_2^4 \ln \nu_2 - \ln\left[x_1 + \frac{m_2}{m_1} x_2\right] + 4x_1^3 x_2 \ln\left[\left(3 + \frac{m_2}{m_1}\right)\Big/4\right] \\ &+ 6x_1^2 x_2^2 \ln\left[\left(1 + \frac{m_2}{m_1}\right)\Big/2\right] + 4x_1 x_2^3 \ln\left[\left(1 + 3\frac{m_2}{m_1}\right)\Big/4\right] + x_2^4 \ln\frac{m_2}{m_1} \end{aligned} \tag{14}$$

Equation (14) has three undetermined constants ($\ln \nu_{1112}$, $\ln \nu_{1122}$, $\ln \nu_{2221}$) and can therefore offer a good deal of flexibility in fitting experimental mixture data. The McAllister 3-body and 4-body models cannot be interpreted rigorously in a thermodynamic sense since the Gibbs activation energy is of arbitrary degree in mole number.

A thermodynamically more rigorous equation can be developed for mixtures based on the Eyring activation energy model. Following equation (9), we let:

$$\Delta G^*_{mixture} = \sum_i \xi_i \Delta G_i^* + \Delta G^{XS} \quad ; \quad \xi_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{15}$$

where we use the concept of q-fraction as the metric for composition dependence. The excess Gibbs energy can be represented in Wohl [n]-suffix form[8] as:

$$\Delta G^{XS} = 2\sum_{i,j} a_{ij}\xi_1\xi_2 + \mathcal{O}(\xi^3) + \cdots \tag{16}$$

where, at present, we neglect [3]-suffix terms and higher. Combining equations (15) and (16) into an Eyring-type expression for the viscosity of a binary system yields:

$$\ln \eta_{mixture} = \xi_1 \ln \eta_1 + \xi_2 \ln \eta_2 - \ln\left[\frac{V_{mixture}}{V_1^{\xi_1} V_2^{\xi_2}}\right] + 2\xi_1\xi_2 C(T) \tag{17}$$

If $V_1 \approx V_2$ and the q-ratio $(q_2/q_1)=1$, equation (17) is identical to the Grunberg-Nissan form. If $V_1 \approx V_2$ and $C(T)=0$, the Yokozeki form is recovered. For $V_1=V_2$, $C(T)=0$ and $(q_2/q_1)=1$, equation (17) becomes the zero-parameter Kendall model. We compare these approximations in the next section.

Results and Discussion

In the present study, we have analyzed the viscosity of three refrigerant/lubricant mixtures: R-22/AB150, R-134a/POE68, and R410A/PVE68. The first mixture is a well known HCFC/oil combination that is used extensively in AC and HP applications. The second combination is typical for HFC usage in AC applications. The third combination involves a new lubricant, polyvinylether, that is under consideration for both AC and HP applications. We have examined the viscosity of this lubricant in mixture with R-410A, a pseudoazeotrope of R-32 and R-125 that is treated as a single component fluid since viscosity data for the separate R-32/PVE68 and R-125/PVE68 mixtures are not presently available.

The viscosity of pure lubricant and pure refrigerant were modeled using the extended Andrade equation[1] to represent the temperature dependence:

$$\ln \eta = A + \frac{B}{T} + CT + DT^2 \tag{18}$$

Experimental viscosity data for AB150, POE68 and PVE68 were collected from available sources[12-15] and least-squares fitted to equation (18) over the experimental temperature ranges. Viscosity data for the refrigerants were calculated using the REFPROP code.[16]

Comparisons of the viscosity mixture models for these three systems, R-22/AB150, R-134a/POE68 and R-410A/PVE68, are shown in Figures 1, 2, and 3, respectively, for a temperature of 40°C. The average deviations at 40°C and over the experimental temperature range are given in Table 1. It is apparent that the zero-parameter models (Arrhenius, Kendall) fail to quantitatively reproduce the experimental mixture data. The one-parameter models (Frenkel, Yokozeki and Grunberg-Nissan) offer a significant improvement in fit, with a slight preference for the Yokozeki model. The two-parameter models (McAllister 3-body), Michels-

Sienel) indicate a small improvement in fit. No further improvement is generally found with the McAllister 4-body model which has three adjustable parameters. Further, the McAllister models can behave erratically when applied to a limited data set since their functional form permits non-physical maxima and minima as illustrated in Figure 3.

The model developed in this work is based on the kinetic treatment of liquids due to Eyring, including effects of non-ideal solution behavior. It is readily extended to multi-component mixtures and can be quantitatively improved through higher order expansions for the Gibbs activation energy. Overall, the accuracy of our two-parameter model is adequate for most engineering applications. Further studies with multicomponent mixtures and with other refrigerant/lubricant combinations are in progress.

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Table 1. Comparison of Viscosity Mixture Models

		Average Error					
		R-22/AB150		**R-134a/POE68**		**R-410A/PVE68**	
Model		T=40°C	-35°C<T<40°	T=40°C	0°C<T<100°	T=40°C	30°C<T<60°
Arrhenius		104.0	825.1	89.3	116.0	75.5	438.0
Kendall		45.5	43.6	61.2	79.0	90.7	91.5
Frenkel	(0)*	10.0	36.9	56.6	65.9	169.9	175.8
	(1)*	-	6.6	-	40.8	-	149.3
	(2)*	-	4.7	-	37.1	-	136.5
Grunberg-Nissan	(0)	10.0	6.1	56.0	39.4	169.9	129.3
	(1)	-	5.1	-	38.9	-	143.4
	(2)	-	4.7	-	36.7	-	136.2
Yokozeki	(0)	3.9	20.3	7.2	23.1	7.4	45.0
	(1)	-	2.5	-	8.5	-	12.3
	(2)	-	2.4	-	8.3	-	11.9
McAllister 3-body	(0)	2.5	60.6	9.8	57.3	26.1	62.3
	(1)	-	8.4	-	14.0	-	28.1
	(2)	-	2.2	-	10.1	-	23.2
McAllister 4-body	(0)	0.2	77.2	3.3	64.3	61.2	61.4
	(1)	-	10.4	-	12.3	-	62.8
	(2)	-	2.3	-	2.2	-	65.5
Michels-Sienel	(0)	4.3	22.1	7.7	18.8	17.6	49.4
(this work)	(1)	-	5.7	-	10.1	-	16.0
	(2)	-	2.3	-	10.1	-	16.1

* (0), (1) and (2) refer to temperature modeling of the adjustable parameters as constants, linear and quadratic in T, respectively.

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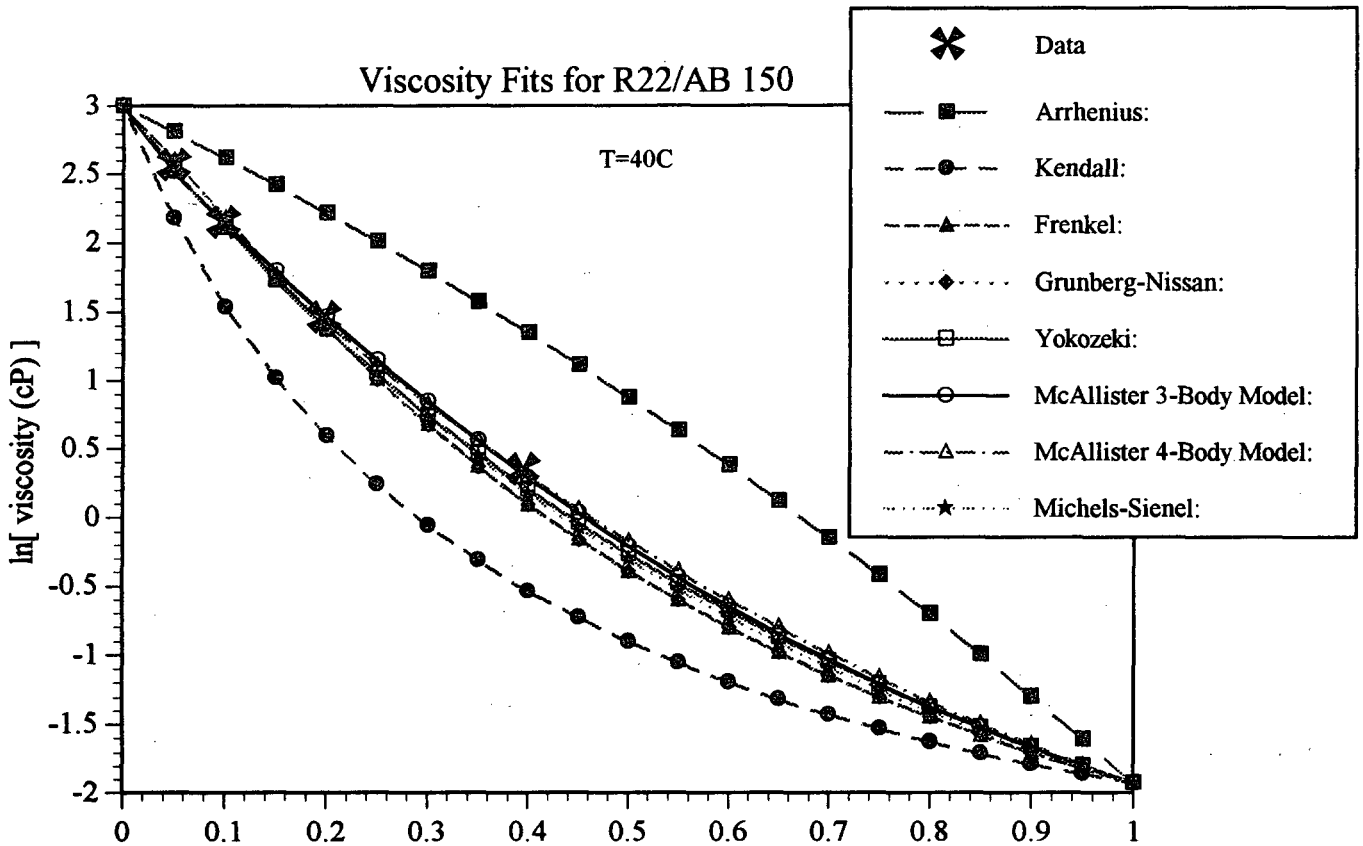

Figure 1 Mass Fraction Refrigerant

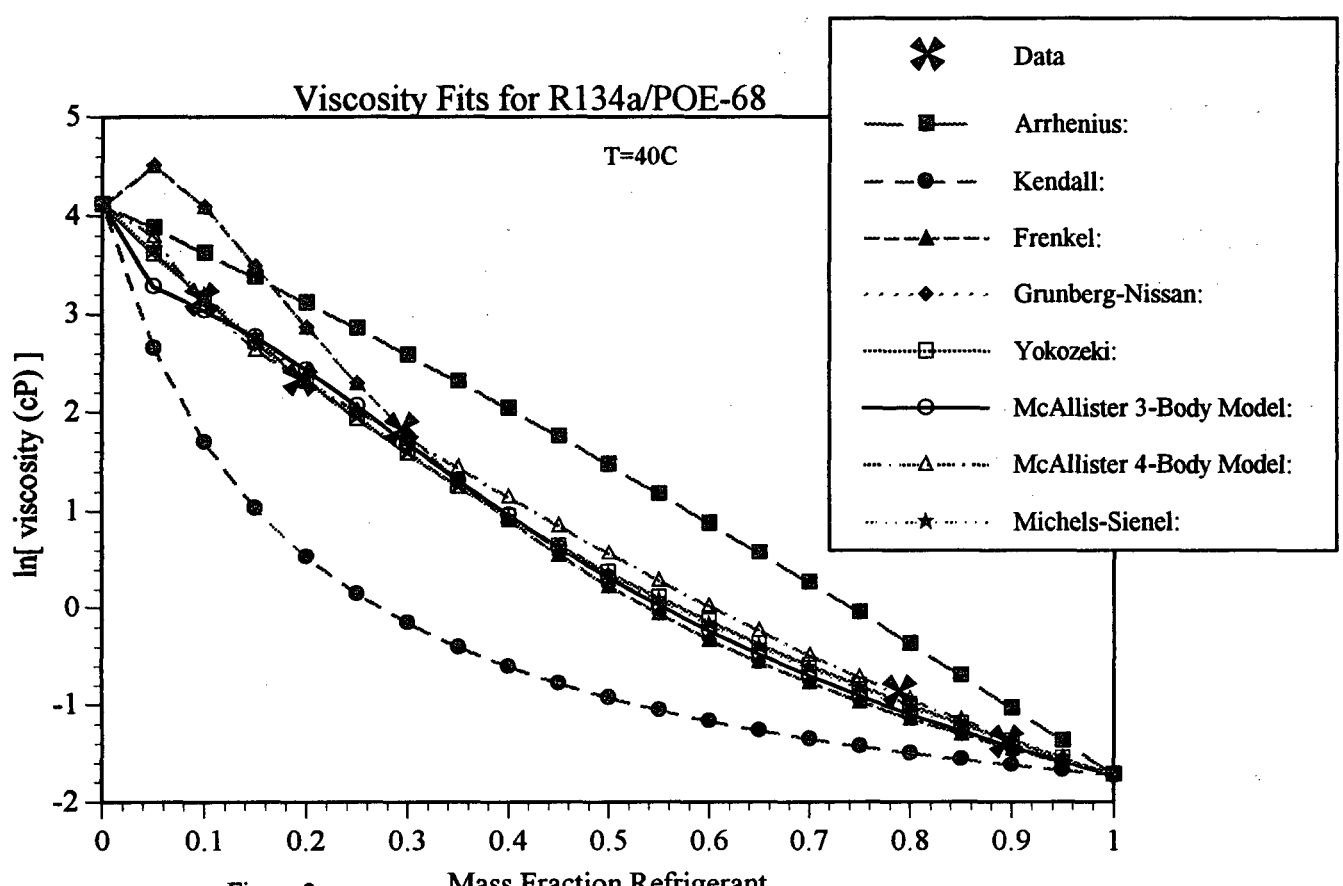

Figure 2 Mass Fraction Refrigerant

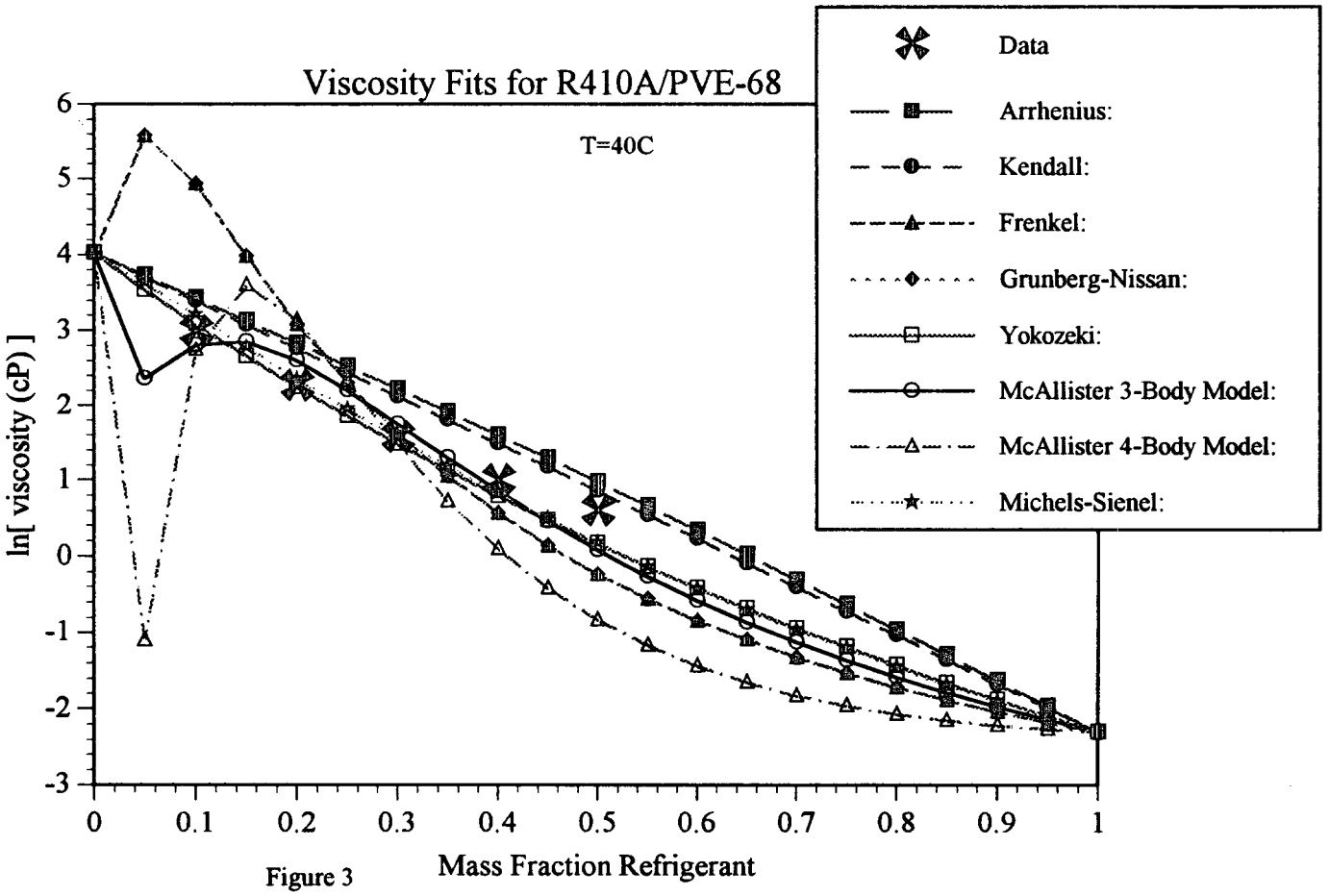
Viscosity Fits for R410A/PVE-68
T=40C
Data
Arrhenius:
Kendall:
Frenkel:
Grunberg-Nissan:
Yokozeki:
McAllister 3-Body Model:
McAllister 4-Body Model:
Michels-Sienel:
ln[viscosity (cP)]
Mass Fraction Refrigerant
6
5
4
3
2
1
0
-1
-2
-3
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Figure 3

INFLUENCE OF HCFC AND HYDROCARBON COMPONENTS IN BLEND REFRIGERANTS ON OIL -REFRIGERANT MISCIBILITY.

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ABSTRACT

Many R-12 and R-22 systems are now being retrofitted to alternative refrigerants, most of which are not fully miscible with mineral oil. To improve oil circulation in retrofitted systems, blend refrigerants containing oil miscible components - chlorofluorohydrocarbons (HCFC) and hydrocarbons (HC) - are often used.

An analysis has been made of the influence of both the quantity and the nature of oil miscible blend components on miscibility with mineral oil. Liquid - liquid equilibrium in oil-refrigerants mixtures was calculated using an equation of state model that was validated with binary experimental data.

Comparison of R-134a based blends showed that FRIGC® FR-12™ containing both an HCFC and an HC has the best oil miscibility.

INTRODUCTION

Faced with the introduction of ozone-friendly HFC refrigerants in new air-conditioning and refrigeration systems, lubricant manufacturers developed a series of new synthetic oils. At the same time, a significant number of existing units, designed for use with R-12 and R-22 refrigerants and mineral or alkylbenzene oils are still in operation. Many of these systems are now being retrofitted to alternative refrigerants, most of which are not miscible with mineral oil to the same extent that would be the case with the original CFC or HCFC refrigerant.

Whereas lower oil miscibility is beneficial for compressor operation, it can be harmful for oil circulation. It is a general understanding that full miscibility of a compressor oil with a refrigerant is desirable to provide reliable oil circulation, and ultimately return of the oil to the compressor. At the same time it is known that oil circulation depends to a great extent on system design and operating conditions and oil can accumulate in certain parts of a system even if it is completely miscible with a refrigerant. There are experimental results showing that sufficient oil circulation can be obtained with refrigerants only partly miscible with oil. In such cases not only liquid-vapor equilibrium but also liquid-liquid equilibrium (LLE) has to be taken into account in order to analyze the operating regimes. Fig.1 illustrates different phase equilibrium types as they are present in a cooling system with partially miscible oil and refrigerant. Two liquid phases can be present in the condenser, the liquid lines and the evaporator.

There are two mechanisms that provide oil carry-over in a system with partial miscibility of the oil and refrigerant.

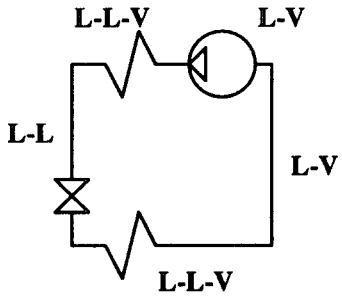


Fig.1. Phase equilibrium types in a cooling system with partially miscible oil and refrigerant.

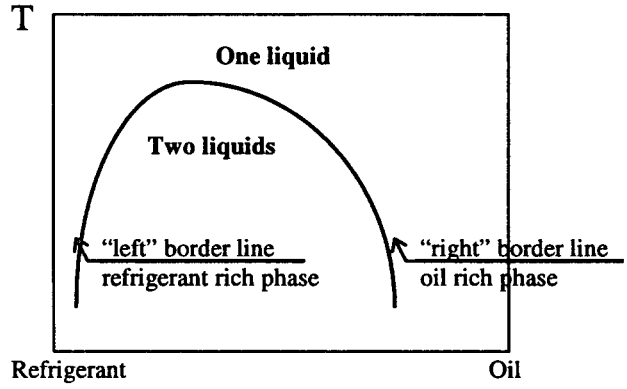


Fig.2. Liquid-liquid equilibrium diagram

First oil moves along the system in a solution with a refrigerant. The maximum quantity of oil that can be carried in this way is determined by the "left" border line as seen on the liquid - liquid equilibrium diagram for the oil-refrigerant mixture (fig.2).

The second way of carrying the oil is the hydrodynamic one. This is when a separate oil-rich liquid phase is forced to move along by the flowing refrigerant. The reliability of this mechanism of oil carry-over can be very high. For example, a proper flow velocity provides oil circulation in vapor (return) lines of most systems by forcing the oil film and the droplets to move with the vapor flow. The efficiency of this mechanism for the liquid lines, and the evaporator, depends on system design as well as the thermophysical properties of the oil-rich and refrigerant-rich phases. The thermophysical property that influences the oil carry-over by this mechanism is primarily the viscosity of the oil-rich phase. It is greatly influenced by dilution of the oil with a refrigerant, since the viscosity of a refrigerant is much lower than that of oil. Hence the viscosity of the oil - refrigerant solution in the case of a partially miscible oil depends on the "right" border line (fig. 2) of the liquid-liquid equilibrium. According to the experimental data, every 5 mass percent of refrigerant soluble in oil lowers the oil viscosity approximately twice. Other factors that improve oil carry-over when the oil is diluted by a refrigerant are densities that are closer for the two liquid phases and a higher foam forming ability of the diluted oil that helps the suction of the foamy oil layer to the return line.

To analyze particular oil-refrigerant combinations for potential oil return problems, it is necessary to have liquid-liquid equilibrium data. Whereas enough experimental data have been collected for one-component refrigerants, similar data for blends are scarce. The situation becomes especially difficult when it is necessary to analyze not just a particular blend but to look at a range of possible concentrations of components. Calculation models are most suitable for this task, however the existing empirical correlations developed for traditional refrigerant-oil pairs are not suitable for generalization, requiring development of new methods.

A calculation model of oil-refrigerant miscibility is presented below, along with some practical results for R-12 substitutes.

METHOD OF CALCULATION

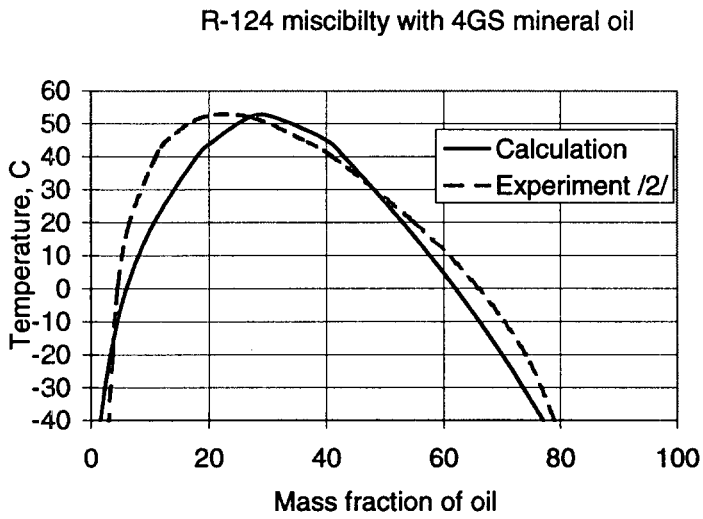
There are two general approaches that can be used to calculate liquid-liquid equilibrium in mixtures of refrigerants with oils. One of them is to use an expression for the excess Gibbs energy for mixtures to obtain the activity coefficients of their components. The other one is to use an Equation of State (EOS) to calculate fugacity coefficients.

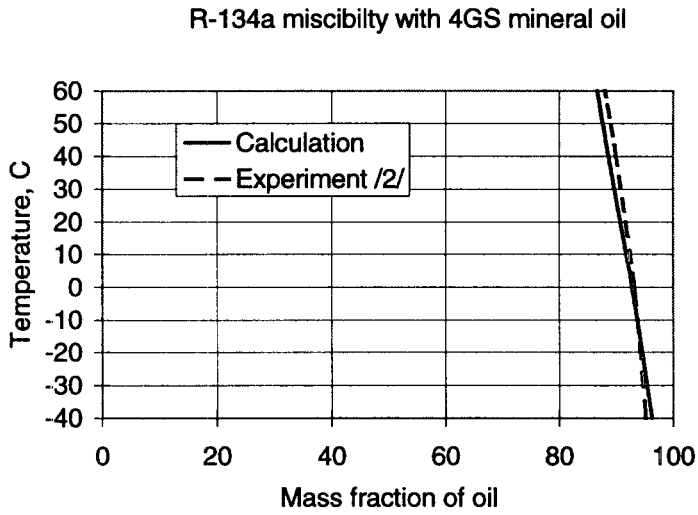
In this work we chose the EOS method taking into account the following considerations: the limited number of available experimental data in the required range of temperatures and concentrations; comparable accuracy of both methods when little experimental information is available; convenience of applying an EOS to multicomponent liquids especially for mixtures containing both low- and high-boiling components; feasibility of using most of the algorithms for liquid-liquid, liquid-vapor and liquid-liquid-vapor equilibria.

A proprietary software was developed that can be used to calculate liquid-vapor and liquid-liquid equilibria in multicomponent mixtures containing up to 10 components (including oils) with the wide range of parameters. Several EOSs of various types are incorporated in the software. One of the problems that was solved is obtaining acceptable convergence of the algorithm to calculate LLE.

There is a special problem when mixtures containing oils are analyzed. It is impossible to determine critical parameters of oils in an experiment due to inevitable decomposition of a sample at high temperatures. In this connection a special method was developed that allows determination of "pseudo-critical" parameters using available data on density, molecular weight and vapor pressure of the oils. The greater the number of available experimental points, the better the accuracy of calculations. As a minimum, only the oil density at one temperature is necessary for the calculations.

The model requires a binary coefficient to be determined for each pair of mixture components using experimental data. To illustrate the accuracy of calculations obtained in this way, the data for refrigerant-oil pairs are presented in fig.3 as a comparison of calculated and experimental border curves. For these examples one binary interaction coefficient was determined for each pair. The agreement can be further improved if temperature or concentration dependent coefficients are used.





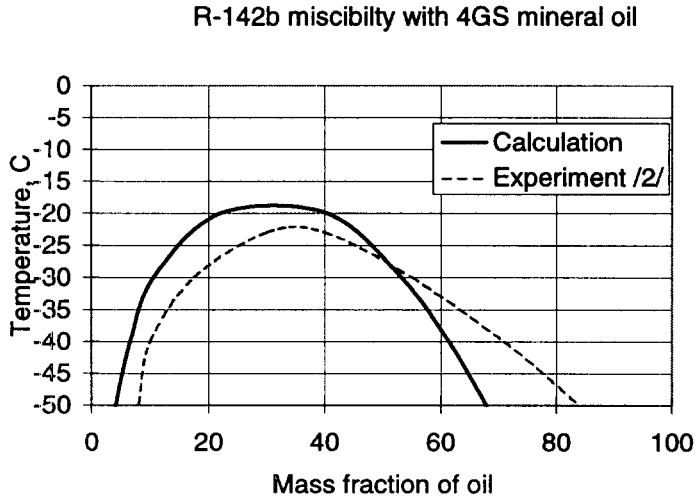


Fig.3. Miscibility of 4GS oil with pure refrigerants.

MISCIBILITY OF MINERAL OIL WITH BLEND REFRIGERANTS

There are two classes of blend refrigerants designed to replace R-12: R-22 based blends and R-134a based blends. Whereas R-22 blends have good miscibility with mineral oils, they have a number of disadvantages such as higher operating pressures, higher glides and poorer material compatibility. R-134a blends offer better operating properties /1/. To offset the low oil miscibility of R-134a, oil-miscible components can be added. They are hydroclorofluorocarbons (HCFCs) and hydrocarbons (HCs). The influence of these components (additives) on oil miscibility is discussed below.

It is well known that addition of an oil-miscible HCFC component improves oil-refrigerant miscibility. Addition of an oil miscible HCFC component shifts both left and right border lines, though the extent of this change is not very big. For example for mixtures of R-134a/R-142b with mineral oil it is necessary to have 5% of HCFC for a 1% miscibility gain in the oil-rich region (fig.4a, table 1).

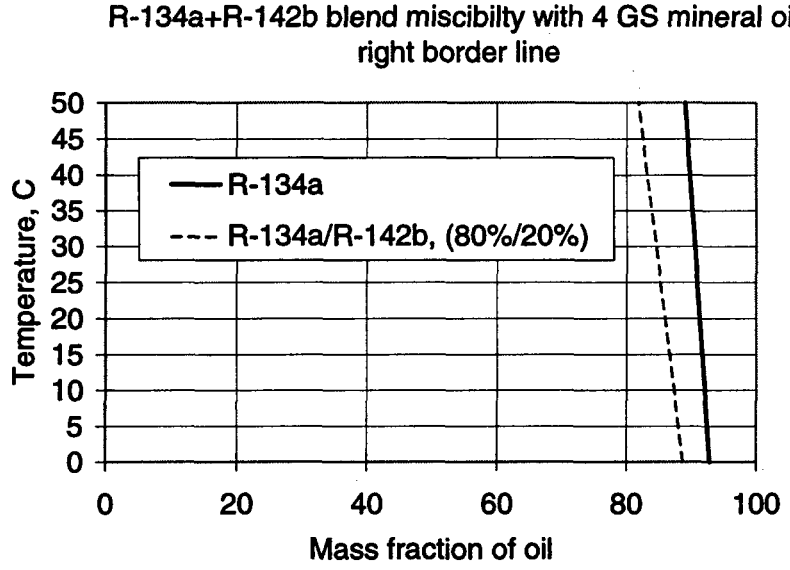


Fig.4a. Right border lines for oil-refrigerants mixtures.

Addition of a hydrocarbon is another way to improve miscibility. At first sight there is no difference between adding an HCFC and a hydrocarbon (HC) since they are comparably miscible with mineral oil. The important difference is that HCs being completely miscible with mineral oil, have big positive deviations from ideal behavior when in solution with HFCs. In fact many HFC-HC pairs exhibit immiscible behavior at lower temperatures forming two liquid phases. This difference translates into an unexpected influence of an HC on oil miscibility for blends containing HFCs. Unlike in the case of HCFCs, the position of the right border line becomes

very sensitive to the quantity of oil in a mixture. The less oil the higher the oil-refrigerant miscibility. Fig.4b illustrates this phenomena for a R-134a/R-600 (normal butane) blend with mineral oil. The concentration of a refrigerant in mineral oil varies by more than 10% depending on the oil quantity in the mixture. For refrigeration systems this is favorable since in most cases the quantity of the oil introduced by the compressor into the system is low (usually not more than 1%-3%) which means improved miscibility for HC containing blends.

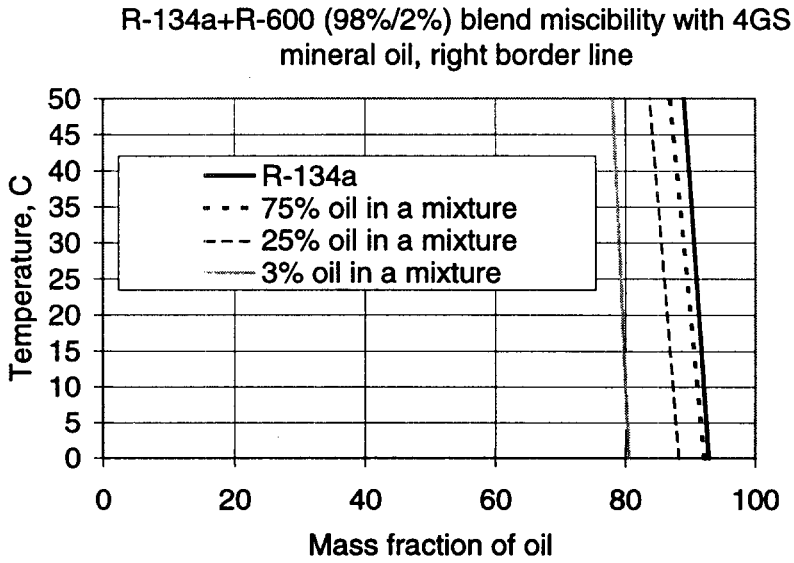


Fig.4b. Right border lines for oil-refrigerants mixtures.

The data presented show that for a low oil content even a small quantity of HC can considerably improve oil miscibility. In fact for a R-134a/R-600 blend, 1% of added R-600 improves miscibility by 6%. This is a 30 fold greater influence than that of an HCFC; introduction of 1% to 2% of butane is equivalent to addition of 20% to 40% of oil-miscible HCFC (R-124, R-142b, etc.). This means that even very small butane additions are very important for proper system operation.

COMPARISON OF REFRIGERANTS

The above considerations, in combination with the calculation method for liquid-liquid equilibrium, were applied for comparison of R-12 alternative refrigerants based on R-134a. In this case, in order to improve miscibility with mineral oil, it is desirable to add more oil-miscible components. At the same time some of the most suitable HCFCs and all HCs are flammable. This puts a limit on the allowed quantity of an additive to ensure its safety. However there may be different approaches to compose a blend in such a situation.

One is to select the most oil-miscible HCFC component acceptable from a thermodynamic viewpoint and add it to the maximum amount acceptable to ensure the blend is nonflammable.

An example of such an approach is a commercially available binary blend of R-134a and R-142b (80% - 20%), where R-142b is an oil-miscible but flammable component. Another approach is to take advantage of the ability of HCs to improve oil miscibility when present even in small quantities as described above. To increase the quantity of an HC, an oil-miscible non-flammable HCFC can be added that serves as a flame retarding component. An example of such an approach is FRIGC® FR-12™ - a ternary blend of R-134a, R-124 and R-600 (59%-39%-2%). The nonflammable component R-124 servers both to improve miscibility and as a flame retarding component to offset flammability of R-600.

Oil miscibility was calculated for these two blends. Fig.4a shows the oil miscibility for R134a/R-142b blend, fig.5 - for FR-12. An HC additive in FR-12 has the same influence as it does in pure R-134a, increasing oil miscibility by more than 10% if oil contents is less then 3%. The data show that FR-12 has more than twice as high miscibility with the oil compared to R134a/R-142b blend.

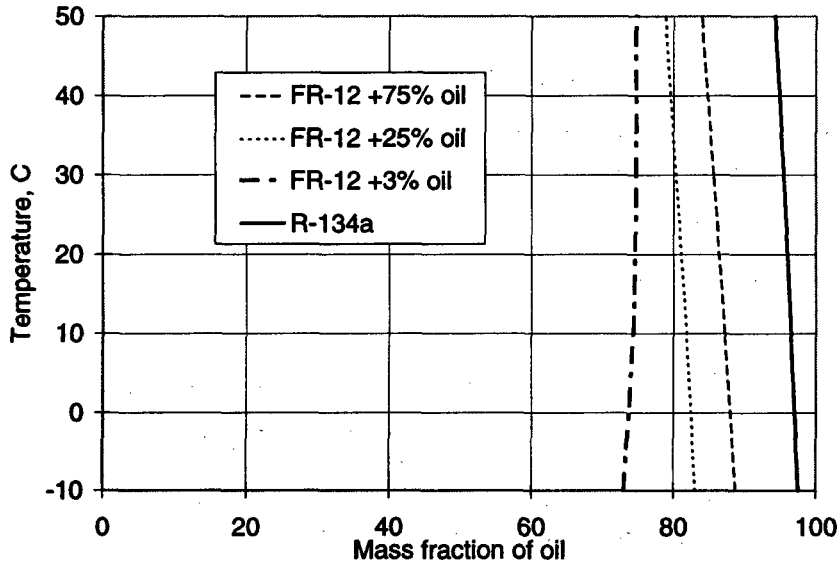


Fig 5. FR-12 miscibility with 4GS mineral oil, right border line.

For practical purposes it is the viscosity of the oil-rich phase that is important for the circulation. Using generated miscibility data, the viscosity of 4GS mineral oil was calculated for typical evaporator conditions when diluted by the refrigerants under comparison. The summary data are presented in the table 1 together with the data for pure 4GS oil for comparison. FR-12 takes advantage of both the HC and HCFC additives and provides the lowest oil viscosity among compared refrigerants.

Table 1. Miscibility and viscosity data for oil-rich phase at evaporator conditions

	Concentration of a refrigerant in **mineral oil**	Viscosity, cSt
4GS, mineral oil @ 40 °C	-	68
4GS, mineral oil @ 0 °C	-	680
R-134a+4GS @ 0 °C	7%	250
R134a/R-142b (80%/20%)+4GS @ 0 °C	11%	150
R-134a/n-butane (98%/2%)+4GS @ 0 °C	19%	50
FR-12+4GS @ 0 °C	27%	20

Another method to improve oil circulation when retrofitting a system is to add some POE oil which is both compatible with mineral oil and miscible with HFCs. Calculations for this case were also performed using the same model. Detailed results for this case are not included in this paper. In general the data show that adding POE increases the mixed oil concentration in the refrigerant. At the same time POE has no significant effect on the dilution of the oil rich phase by a refrigerant. In this regard HC and POE are complimentary additives, each influencing a different border line (fig. 2) but both improving the mutual miscibility of refrigerants and oil. At the same time adding a POE to a mineral oil will proportionally decrease the amount of mineral oil introduced into the system by the compressor thus decreasing the requirements for the refrigerant-oil miscibility. As experiments show /3/, FRIGC FR-12 with 70%-30% mixture of a mineral oil/POE can provide oil circulation almost identical to that with original R-12 with mineral oil even at very low evaporator temperatures down to -20 °C.

CONCLUSIONS

- Adding an HCFC or an HC to a blend refrigerant improves its miscibility with a mineral oil.
- The influence of an HC additive is much greater than that of an HCFC. Introduction of 1%...2% of butane is equivalent to addition of 20%...50% of oil-soluble HCFC (R-124 or R-142b).
- The combined HC and HCFC additives can decrease viscosity of oil down to acceptable levels at evaporator temperature.
- HCs and POE are complimentary additives, each influencing different border line, both improving the mutual miscibility of refrigerants and oil.
- FRIGC FR-12 provides the highest oil miscibility among the R-134a based refrigerants.

ACKNOWLEDGMENTS

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EXPERIMENTAL ASSESSMENT OF OIL RETURN WITH CFC AND HCFC ALTERNATIVES

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ABSTRACT

CFCs & HCFCs have mostly been used with mineral oils.
Alkylbenzene type lubricants have usually been preferred when HCFCs were either used at low temperature and/or as HCFC/HFC based refrigerants.
The Refrigeration & A/C Industry has systematically favored miscible lubricants ; consequently, polyolester, polyalkylene glycol and recently polyether lubricants have been introduced on the market.
This industry, especially people operating on the field, are today quite confused about the best selection for oil/refrigerant.
In this article, the study goes beyond the study of the miscibility between the refrigerant and the oil which is only one parameter to decide on oil type to adopt. The influence of other important factors such as solubility of the refrigerant into the oil, oil fluidity are also deeply investigated...
The aim of this paper is to detail upon application & technology and refrigerant/oil type used what can be accepted and what will lead to compressor failure.

INTRODUCTION

Miscibility between refrigerants and lubricants has long been considered essential to the refrigeration cycle. Consequently many lubricant types have been developed for hydrofluorocarbons (HFC) in order to fully satisfy this criterion.

However many systems run with R-22/mineral oil without any problem, especially in commercial and air conditioning application, even though miscibility is only partial.

Indeed, even if the refrigerant is not miscible with the lubricant, refrigerant vapor can dissolve in the oil causing a drop in its kinematic viscosity. Since the viscosity of the oil/ refrigerant is the major factor determining the oil return to the compressor, solubility of refrigerant and temperature level are therefore quite important parameters to take into account.

In addition, experiments to evaluate directly the oil return rate have been carried out and the results, as well as the set up itself, are shown. The aim of this paper is to detail upon application/technology and refrigerant/lubricant type used, how to choose the optimal lubricant.

TEST FACILITY

The ability of refrigerants to carry along the lubricant at constant volumetric flowrate is measured with the test equipment shown in Figure 1.

A copper tube 2.4 m in length and 8 mm internal diameter is wound into a coil of 4.5 turns, each of 17 cm diameter. A specified amount of the sample oil placed in the tube is kept at a fixed temperature whilst liquid refrigerant is passed through the tube at an outlet vapour flowrate of 1 cu.m/hr at 20°C/68F @ 1 atm.

The mixture of oil and refrigerant is recovered at the tube outlet, and after the refrigerant has been evaporated, the weight of the oil remaining is measured.

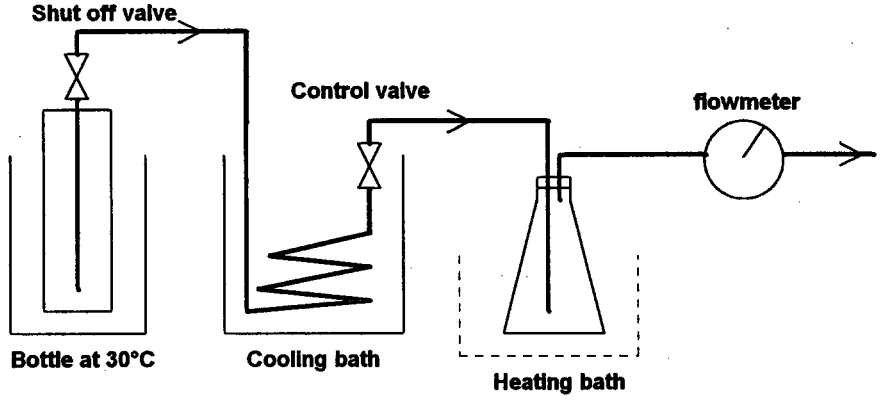

Figure 1 : Testing device for oil return measurement

TEST RESULTS AND DISCUSSION

The experiments were carried out with two types of refrigerant/lubricant combinations. The first set of data concerns the retrofit application in refrigeration. Three alternative blends commonly found on the market have been compared to R-12 & R-134a. In this case, original lubricant (Mineral oil) has been used. The second set of data concerns the air conditioning application. Actual candidates have been evaluated refering to R-22.

Refrigeration Application

R-12 has been traditionaly used with mineral oil in refrigeration application at evaporating temperature as low as -30°C/-22F.

During retrofitting the need to change the lubricant is often a key issue. The following results overview the performances of three so-called "drop-in" replacements, FORANE® FX 56 (R-409A) and two other blends known as blend S and blend I. The mineral oil used (SUNISO 3GS) is commonly found in refrigeration systems.

The miscibility of these blends with the lubricant is represented in Figure 2.

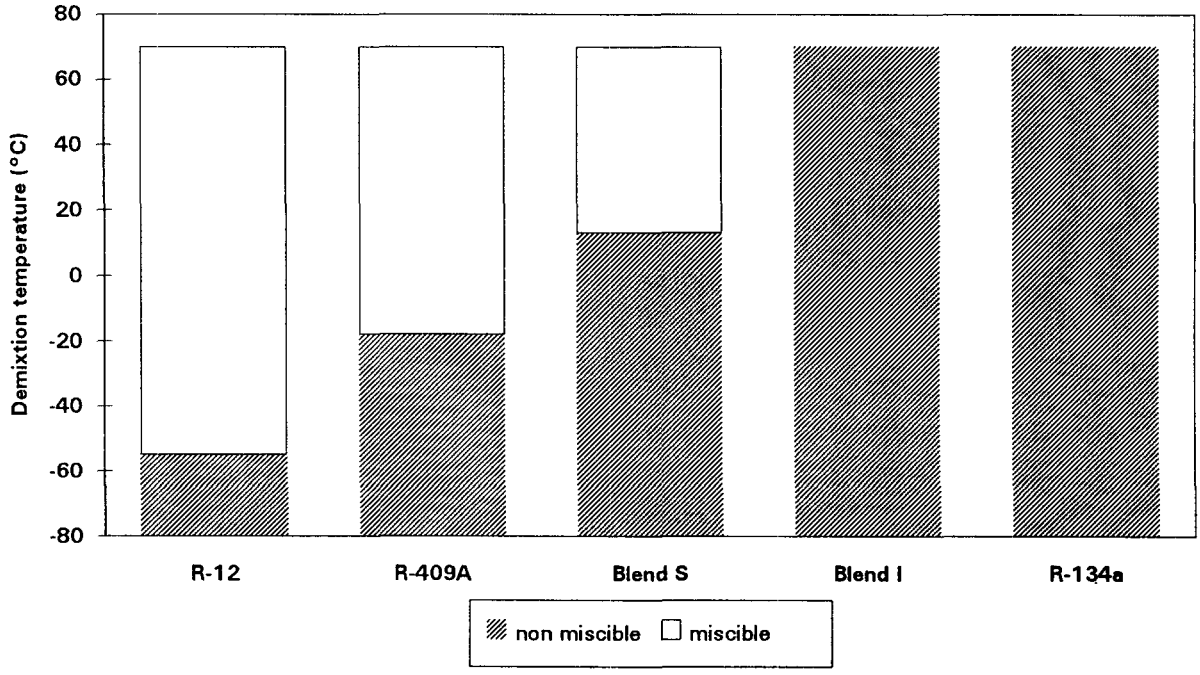

Figure 2 : Miscibility data at 10 % wt of oil in refrigerant

For a 10 % wt of lubricant in refrigerant, two areas are plotted : the white area corresponding to a fully miscible mixture and the dashed one corresponding to the separation of the oil and liquid refrigerant phases.

Since blend I and R-134a are hydrofluorocarbons (HFC), they are totally non miscible with mineral oil. Blend S, R-409A and R-12 exhibit various degree of miscibility.

In order to evaluate the solubility of gaseous refrigerant in lubricant, experiment consisting to measure the vapor pressure of different refrigerant/oil mixtures has been performed.

Results obtained with Suniso 3GS are plotted in Figure 3.

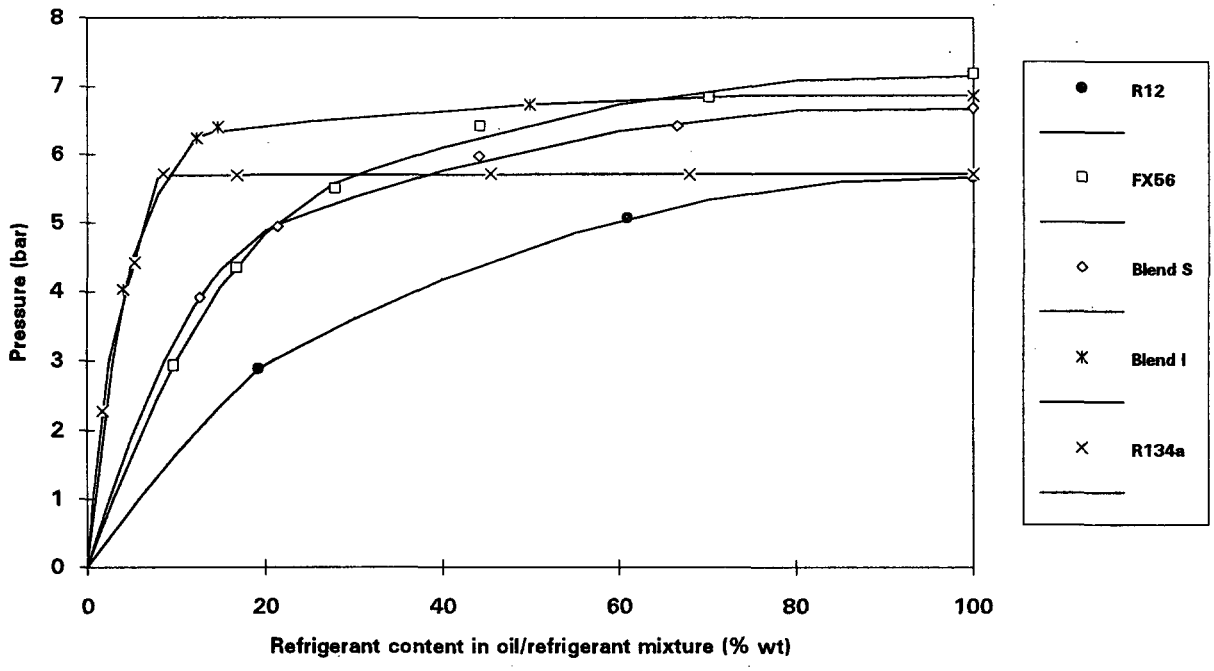

Figure 3 : Solubility of R-12 alternatives in Suniso 3GS at 20°C/68F

For example, the solubility of the refrigerant at a section line of 20°C is reported in Table 1.

Evaporating temperature	-30°C		0°C	
Refrigerant	Suction pressure bar	Solubility % wt	Suction pressure bar	Solubility % wt
R-12	1	6	3	21
R-409A	1	2.9	3	10
Blend S	1	2.5	3	9
Blend I	1	1	3	3
R-134a	1	0.7	3	2.5

Table 1 : Solubility of refrigerant in Suniso 3GS at 20°C/68F

It can be observed in both Figure 2 and Table 1, three kinds of behavior : A high solubility of R-12 in mineral oil, in accordance with the large miscibility area ; a medium solubility of R-409A and blend S corresponding to a lower miscibility of those refrigerants with mineral oil and a low solubility of Blend I and R-134a due to their total non miscibility with this type of lubricant.

In order to better simulate the refrigerant/oil mixture behavior in an evaporator, return oil experiment has been carried out at - 30°C/-22F.

Figure 4 below summarizes the results.

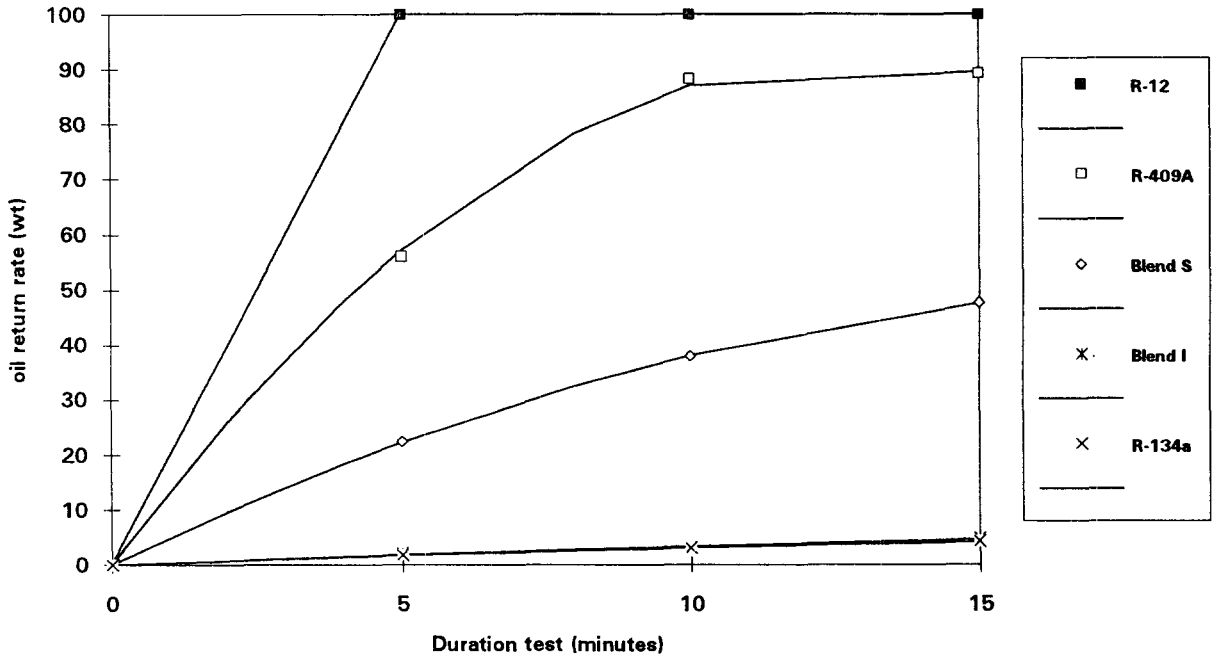

Figure 4 : Oil return rate with Suniso 3GS at -30°C/-22F

It can be seen that the oil return with liquid refrigerant is highly dependent on miscibility as indicated by the following :

- Full and immediate oil return is obtained with R-12 (5 mins)
- Near complete (90 %) oil return occurred with R-409A after 10 to 15 minutes
- The return rate observed with blend S is twice as small as that of R-12 (50 % at 15 mins)
- Very low oil return rates (< 5 %) are measured with blend I and R-134a even after 30 mins elapsed time.

Air conditioning application

Today, the main R-22 substitutes in air conditioning application are identified and the best candidates are HFC based blends, R-407C, R-404A and R-410A.

At the same time, polyolester (POE) lubricants were developed to achieve the required miscibility with these solutions. But in some cases, fully miscible POE lubricants in combination with HFC refrigerants seemed to fail due to high friction in the compressor. Lubricants with poorer miscibility but better anti-wear properties could be developed to solve this problem out as it was the case with paraffinic lubricant type and R-22.

Since Air Conditioning application requires higher evaporating temperature, the use of lower miscible lubricant/refrigerant mixture can be considered.

The following Figure illustrates this particular point.

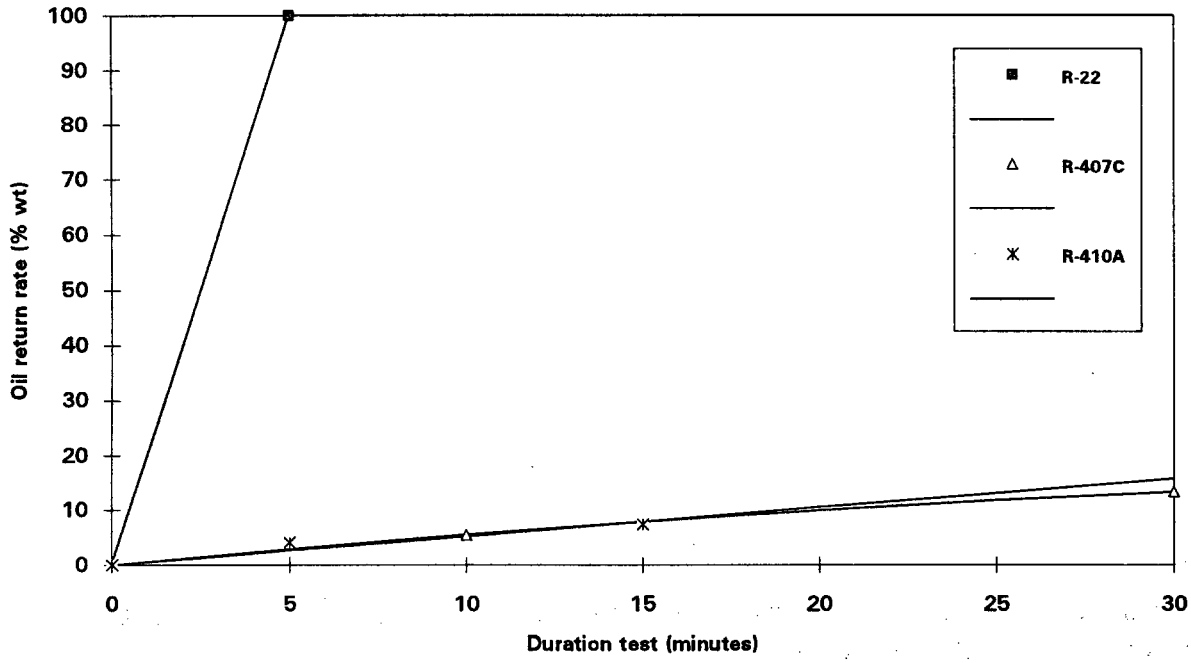

Figure 5 : Influence of the temperature on the oil return

The same experimental procedure as previously described was used to quantify the oil return rate with R-407C and R-410A and SUNISO 3GS (MO1). The experiment was carried out at -10°C/14F and a non negligible rate (> 10 %) has been observed, unlike that of obtained with R-134a and the same oil at -30°C/-22F (< 5 %).

However, a 10 % oil return rate, is still not enough to ensure a good lubrication.

Differents kinds of synthetic lubricants ; alkylbenzene (AB), polyolester (POE1, POE2) and polyvinylether (PVE) have been evaluated with HFC based blends.

Figure 6 represents the miscibility data of R-407C with these lubricants at a 5 % wt ratio.

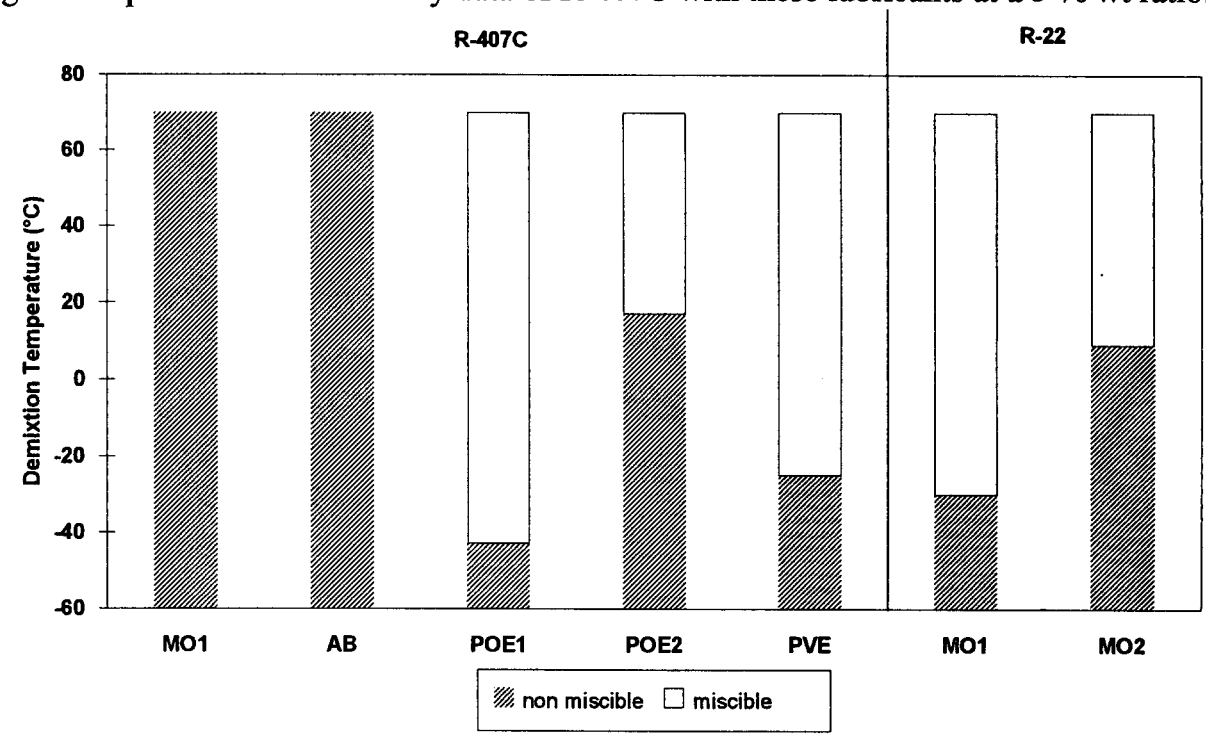

Figure 6 : Miscibility data at 5 % wt of oil in refrigerant

POE1 was initially developed to satisfy a full miscibility with R-407C and is comparable to MO1 with R-22. POE2 and PVE exhibit lower miscibility with R-407C but higher lubrication like paraffinic mineral oil (MO2) and R-22.

Same experiment of solubility, consisting to measure the vapor pressure of oil/ refrigerant mixtures, has been carried out.

The table 2 summarizes the results obtained at 20°C/68F and a suction pressure corresponding to a standard A/C evaporation (7°C/45F).

Lubricant	Refrigerant	Suction pressure bar	Solubility % wt
MO1	R-22	6	19
MO2	R-22	6	14
AB	R-407C	6	6
POE1	R-407C	6	19
POE2	R-407C	6	16
AB	R-404A	7.5	7
POE1	R-404A	7.5	22
POE2	R-404A	7.5	17
AB	R-410A	9.5	4
POE1	R-410A	9.5	23
POE2	R-410A	9.5	17

Table 2 : solubility of refrigerant in lubricant at 20°C/68F

Although miscibility of HFC blends are only partial, POE2 exhibits interesting behavior with a solubility as good as the ones obtained with POE1.

In order to confirm these good results, oil return experiments were performed with the differents lubricants and refrigerants. Results are reported in Figure 7.

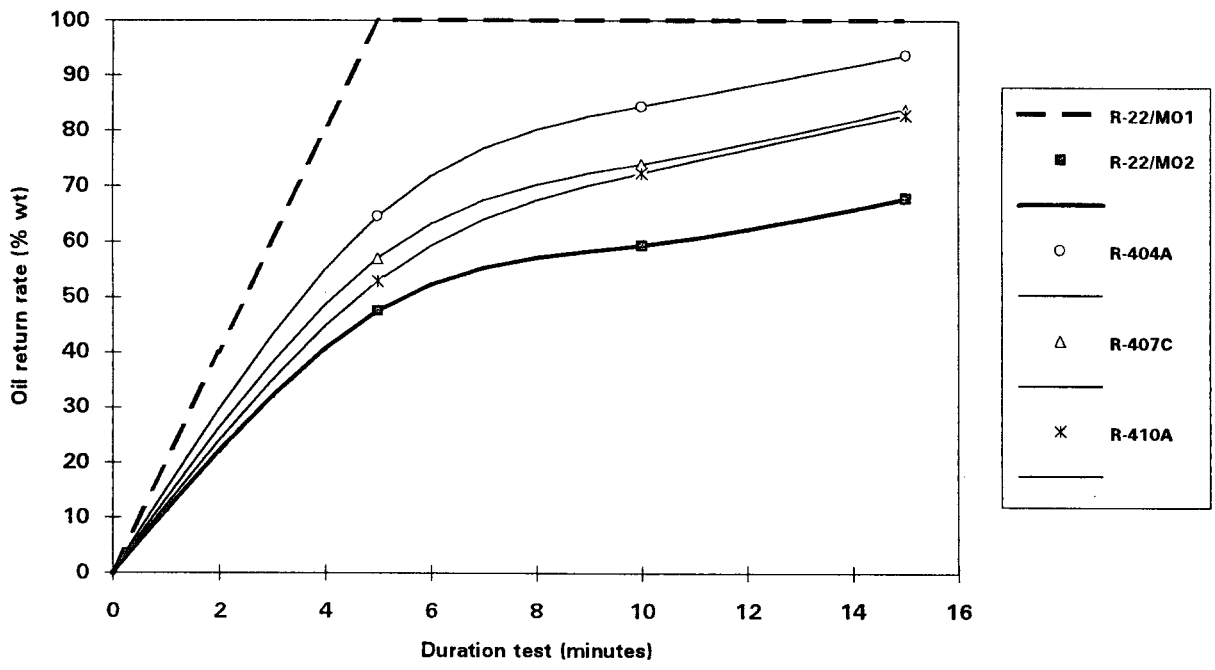

Figure 7 : Oil return rate with POE2 at -10°C/14F

- Quantitative and immediate oil return rate is observed with all the HFC refrigerants and POE1, like R-22 and MO1.

- Low oil return rate is obtained even after 15 minutes (< 20 %) with AB.

- As shown by Figure 7, near complete oil return occurred with HFC refrigerants and POE2. Compared to R-22/MO2 which is considered as acceptable in term of oil return, the POE2/HFC refrigerant combinations have a better behavior.

CONCLUSION

Even if the miscibility of oil and refrigerant is only partial, it is possible to reach good refrigerant gas solubility and oil return rate. But attention should also be paid to the system type involved, and the system design (compactness, refrigerant flowrate, tubing length, lubricant traps...)

From this study, it can be pointed out that oil return is more related to miscibility at low temperature applications than at high/medium temperature. The evaluation of the gas solubility in oil and the oil return can help in the selection of the optimal lubricant depending on the application and the technology considered.

TRANSPORT REFRIGERATION WITH A TRANSCRITICAL REFRIGERATION CYCLE USING CARBON DIOXIDE AS REFRIGERANT

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ABSTRACT

Carbon dioxid is a natural refrigerant with negligible global warming potential. It is non-poisonous and non-flammable, and recycling is not necessary, which means that service and maintenance are easy. To demonstrate the feasability of carbon dioxide as refrigerant for transport refrigeration, a laboratory prototype was tested according to the German standard DIN 8958 "Testing of cooling equipment for insulated means of transportation" [1]. The cooling capacity was measured in a calorimeter test cell. At a constant ambient air temperature of 30 °C (86 °F) the temperature of the cold room was varied between -20 °C (-4 °F) and 12 °C (54 °F). The operating conditions for the laboratory prototype (especially regarding the maximum compressor discharge temperature and pressure) stayed in an acceptable range, even for ambient air temperatures up to 47 °C (117 °F). The measurement results are presented and discussed, and the potential of further improvement is pointed out. In addition, components of the transcritical cycle are discussed. Measurement data were compared with data of other transport refrigeration units measured and certified by the German TÜV. The laboratory test results show that carbon dioxide is an interesting alternative refrigerant for future transport refrigeration applications.

INTRODUCTION

Carbon dioxide was used as refrigerant since the last century up to the 1930s when the CFCs occure on the market. But the CFCs were recently identified as potential major "ozone killers". The 1987 Montreal Protocol mandated the phase out of the CFCs. So in the early 1990s the automotive industries replaced CFC-12 by HFC-134a in mobile air conditioning systems. The HFCs have no ozone depleting potential (ODP) but they still have a high direct global warming potential (GWP). Hence, reseach activities (especially in Europe) try to introduce the natural substance carbon dioxide as refrigerant for future mobile air conditioning systems [8]. However, refrigerated trucks (a fleet of about one million vehicles [2]) cannot use HFC-134a as refrigerant, because of the low cooling capacity at lower evaporation temperatures. As alternatives for the ozone depleting refrigerants R-502 and HCFC-22 several options of zeotropic and azeotropic blends are commercially available. Currently available options for both retrofits of the existing fleet and new equipment of about 100,000 units per year are bewilderingly large [2]. In new equipment refrigerants with no ODP and low GWP should be used. The near azeotropic blend R-404A and the slightly different azeotropic R-507 are used preferably in new truck units. Table 1 compares refrigerant properties of the old refrigerants CFC-12, R-502, and HCFC-22, the new promising blends R-404A, R-507, R-410A, and the natural refrigerant CO_2. All of the new blends contain considerable portions of flammable components. The GWPs of these blends are still higher than that of HFC-134a. Direct refrigerant emissions from truck refrigeration units were estimated to about 20 percent of the charge per year [2].
In contrast to that, carbon dioxide is a natural substance and part of the earth's carbon cycle. It does not need to be especially produced. It is available worldwide at a low price from natural wells or as an industrial by-product. Hence, it has no net global warming

potential. It has well documented properties, no unknown harmful breakdown products with long-term effects. Carbon dioxide is non-flammable, and non-poisonous. Since no recovery and recycling is necessary, it is easy to handle in service and maintenance.
For this reasons carbon dioxide is suggested as a future option for transport refrigeration [2, 3]. 1997 KONVEKTA started research in this area, based on over one thousand operating hours of experience with CO_2 as refrigerant in mobile air conditioners both in the laboratory and on-the-road.

DESCRIPTION OF THE PROTOTYPE SYSTEM

Carbon dioxide has a high critical pressure of 73.8 bar (1070 psi) and a low critical temperature of 31.1 °C (88 °F) compared to the other refrigerants (see Table 1). As a consequence, refrigeration units using carbon dioxide as refrigerant usually operate in the so called "transcritical cycle" (see Figure 1) with a high-side pressure above the critical pressure. At supercritical conditions the pressure is independent of the temperature, and no phase change occures. Hence, the heat rejection heat exchanger in the transcritical cycle usually is called "gas cooler" instead of "condenser". Due to the supercritical conditions the pressure of the gas cooler is not determined by the ambient air temperature but by the refrigerant charge. However, there is an "optimum" high-side pressure for an optimum COP. This optimum pressure can be estimated with the help of a graphical method given by Inokuty [5, 6], and also described by Bhatti [7]. According to this method, a tangent is drawn to the isotherm of the gas cooler exit CO_2 temperature starting from the point of intersection of the 90% quality line and the suction pressure line on the pressure enthalpy diagram of carbon dioxide (see Figure 1). The point where the tangent touches the isotherm determines the optimum pressure for the theoretical cycle. The theoretical COP is defined as the ratio of the enthalpy difference q divided by w. Wertenbach et al. [8] showed the dependence of the gas cooler refrigerant outlet temperature on the optimum high-side pressure for a mobile air conditioner.

The laboratory prototype presented in this paper was designed as an independend truck refrigeration unit of about 4000 Watts cooling capacity in the electric mode. The unit has a seperate Diesel engine with a generator. If electric power is available at the parking place the unit can be operated with an electric motor in order to reduce noise emission. The unit has a standard electric defrost and heating system for the evaporator. The truck unit is a so called "split unit", which means that evaporator and expansion valve are installed in an insulated box. All other parts are placed usually outside in front of the box and above the truck driver's compartment. The major components of the laboratory refrigeration system are shown in Figure 2. Basically the system consists of only four important parts: the compressor (2), the gas cooler (1), the expansion valve (4), and the evaporator (3). Based on good experiences on-the-road and in the laboratory [4, 9, 10, 11] with such a system for bus air conditioners a similar system was also designed as truck refrigeration prototype. Only the heat exchangers and the refrigerant charge were modified for the particular application. The system does include neither a receiver nor an internal heat exchanger. The entire prototype including all components was designed according to the German regulations for pressure vessels [12]. The high pressure side was equipped with pressure safety valves that open at operation pressures of about 140 bar (2030 psi). Conduits for component connections included rigid and flexible steel tubes. The refrigerant charge of the unit was 1.95 kg (4.3 lb) carbon dioxide.

LABORATORY TESTS

Refrigerant and air temperatures were measured by thermocouples, and refrigerant pressures by transducers with semiconductor diaphragm pressure sensors. The cooling capacity was measured in a calorimeter test cell with a procedure based on the regulations of German Industrial Standard for testing cooling equipment for insulated means of transportation [1]. The evaporator and expansion valve were installed in an indoor simulation box. All other parts were placed in a room where ambient conditions were maintained. The insulated box was heated by electrical resistance elements. All test data were recorded by a logging and processing system during a steady-state test period of about three hours.

The indoor temperatures varied between -20 °C (-4 °F) and 12 °C (54 °F). The ambient temperatures varied between 30 °C (86 °F) and 47 °C (117 °F). The measured suction pressure was in a range between 11.9 bar (173 psi) and 32.4 bar (470 psi), the discharge pressure varied between 81.6 bar (1183 psi) and 115.5 bar (1675 psi), with a corresponding compression ratio range between 2.88 and 6.86. In most conditions the high-side pressure was near the optimum pressure. For example: with a gas cooler exit temperature of 30.6 °C (87 °F) and an evaporation pressure of 11.9 bar (173 psi) Inokuty's method yields an optimum pressure of about 81 bar (1175 psi) which is very close to the measured value of 81.6 bar (1183 psi). The optimum pressure given by Wertenbach et al. [8] is slightly lower due to higher evaporation pressures in mobile air conditioning systems.

The compressor of the system was derived from a factory-produced open type reciprocating compressor BOCK FKX 3. Hence, the outer shape of the CO_2-compressor is the same as that of the standard compressor. Except of the crankshaft, all major parts of the compressor were reinforced. The compressor had two cylinders arranged in line with a bore of 28 mm (1.1 inch) and a stroke of 49 mm (1.93 inch). Hence, the displacement was reduced from originally 233 cc to approximately 60 cc (3.66 in^3). The compressor was equipped with a gear pump for forced lubrication. The same high-viscosity oil as in the CO_2 bus air conditioning applications was used. Compressor indicator diagram measurements show high compressor efficiencies (see Köhler et al. [4, 11]). The measurements in the calorimeter test cell showed low total power consumptions and discharge tempertures below 145 °C (293 °F). This indicates high indicated shaft efficiencies while indicated volumetric efficiencies might be lower compared to values published in [4] and [11] due to lower evaporation pressures and the increasing influence of the clearence.

The refrigeration unit was equipped with a commercially available EGELHOF electronic expansion valve. The valve has proofen reliability for bus air conditioning during several hundred running hours on-the-road. The tests with the truck refrigeration unit showed that during all operation conditions the superheat was about 6 K.

The evaporator and gas cooler were designed as fin-and-tube heat exchangers similar to those used in standard R-404A or R-507 units. Exept the 10 mm (3/8") diameter tubes were made of steel instead of copper to withstand the higher pressures. So weight, size and cost of the prototype are comparable to standard refrigeration units. The number of circuits in both heat exchangers had been reduced due to the higher gas density of carbon dioxide. The refrigerant pressure drop in both heat exchangers was in the order of 1 bar (15 psi). The average gas cooler efficiency, defined as refrigerant side temperature drop divided by the difference of the refrigerant inlet temperature and air inlet temperature [7], was about 0.94. The temperature glide of carbon dioxide in the near critical region is similar to

temperature glides of zeotropic blends during condensation. The measured temperature distribution in the evaporator shown in Figure 3 indicates a constant evaporation temperature and a superheat area of about 40 percent. The difference between air temperature and refrigerant temperature is about 8 to 10 K. The evaporator could be optimized by increasing the heat exchanger's air-side surface. The tube diameter could be reduced with an increasing number of refrigerant circuits. For the same reasons the gas cooler could also be reduced in size. An internal heat exchanger in the suction line as it is standard in most commercially available transport refrigeration units would shift the superheat area from the evaporator to the internal heat exchanger. This might give additional benefits for the carbon dioxide system.

COMPARISON

All data of the compared units were measured according to the standard DIN 8958 conditions [1]. Typical technical data of the independent truck transport refrigeration units A, B, C, and D are given in Table 2. For better comparison of the COP all units operated in the electric mode. Units A, B and C were tested by the German TÜV. Units A and B (equipped with identical evaporators) used the CFC-blend R-502 with a charge of about 5 kg (11 lb). Unit A ran with a higher compressor speed to increase the cooling capacity (see Figure 4). Unit C was charged with 4 kg (8.8 lb) of the alternative HFC-blend R-507 while unit D was charged with 1.95 kg (4.3 lb) carbon dioxide. Unit C and D had comparable evaporator air-side surfaces and compressor speeds. The CO_2- compressor had only about a quarter of the displacement of the HFC-compressor. But the CO_2-unit had a higher cooling capacity. The cooling capacity and the efficiency of unit A was the highest. For this reasons unit A was selected as baseline for the comparison. Unit B had 86 % of the compressor speed and 55 % to 76 % of the cooling capacity of unit A. The R-507 transport refrigeration unit C had a compressor speed of 69 %, an evaporator air-side surface of 63 %, and a cooling capacity between 42 and 51 % compared to unit A. The carbon dioxide system (unit D) had a compressor speed of 72 %, a displacement of 26 %, an evaporator air-side surface of 56 %, and a cooling capacity between 59 and 70 %. The overall coefficients of performance (COP) are depicted in Figure 5 in relation to the COP of baseline unit A. Due to throttling effects the COP of unit B is in the range of 97 % (at -20 °C / -4 °F) and 77 % (at 0 °C / 32 °F) compared to the COP of unit A. The relative COP of the R-507 unit C is between 70 and 75 % due to the reduced evaporator size. Unit D with the smallest evaporator which used carbon dioxide as refrigerant had relative high COPs. The COPs of the CO_2-unit were about 15 % lower than the COPs of the baseline unit A, but about 18 % higher than the COPs of the R-507 unit C.

The theoretical performance of the new HFC-blends R-404A, R-507 and R-410A show about 5 percent losses in COP compared with R-502 [2]. The COP of a carbon dioxide system is expected to be even lower due to the transcritical cycle. The real performance data depend strongly on the design of the refrigeration unit. Bivens and Yokozeki [13] pointed out some reasons for the discrepancy between theoretical calculated COP and measurement data for R-410A compared with HCFC-22. They mentioned higher compressor efficiencies due to lower pressure ratio, and lower suction line pressure drop and higher heat transfer coefficients due to higher densities. The same reasons apply for carbon dioxide. The benefits of CO_2-systems due to low suction line pressure drops were discussed by Köhler and Sonnekalb [14]. The zeotropic blend R-410A has higher operating pressures (up to 40 bar or 580 psi) than R-502 and the other refigerants listed in Table 1 except carbon dioxide. But its contribution to global warming when released to the

atmosphere is even higher than that of HFC-134a and HCFC-22. As a consequence, the authors suggest that the natural refrigerant carbon dioxide be used instead in future high-pressure transport refrigeration systems.

CONCLUSION

Measurement data of a prototype transport refrigeration system with the natural refrigerant carbon dioxide in transcritical cycle conditions show a similar overall energy efficiency compared with HFC-systems and CFC-systems of the same cooling capacity. In mobile applications leakage rates up to 20 percent of charge per year is not unusual, and all CFC-alternatives have high GWP values. Therefore future high-pressure transport refrigeration systems with CO_2 would not increase power consumption but reduce the GWP impact. The tested CO_2 unit had the same size and weight as a standard HFC-system. In addition, recovery and recycling is not necessary for carbon dioxide used as a refrigerant which makes service and maintenance very easy.

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Refrigerant	MW)[1]	NBP)[2] (°C)	T_C (°C)	P_C (MPa)	LFL)[3] (%)	at. life (years)	ODP	GWP 100 yr
CFC-12	120.91	-29.8	112.0	4.11	none	102	1.0	8500
R-502	111.64	-45.4	82.2	4.08	none		0.283	5591
48.8% HCFC-22	86.47	-40.8	96.2	4.99	none	13.3	0.055	1700
51.2% CFC-115	154.47	-39.1	79.9	3.15	none	1700	0.6	9300
HCFC-22	86.47	-40.8	96.2	4.99	none	13.3	0.055	1700
HFC-134a	102.03	-26.1	101.1	4.06	none	14	0	1300
R-507 (AZ-50)	98.90	-46.7	70.9	3.79	none		0	3800
50% HFC-125	120.02	-48.1	66.3	3.63	none	36		3200
50% HFC-143a	84.04	-47.4	73.6	3.83	7.4	55		4400
R-404A (HP62, FX-70)	97.60	-46.5	72.1	3.73	none		0	3748
	120.02	-48.1	66.3	3.63	none	36		3200
44% HFC-125	84.04	-47.4	73.6	3.83	7.4	55		4400
52% HFC-143a	102.03	-26.1	101.1	4.06	none	14		1300
4% HFC-134a								
R-410A (AZ-20)	72.56	-50.5	72.5	4.96	none		0	1890
50% HFC-32	52.02	-51.7	78.2	5.80	14.0	6		580
50% HFC-125	120.02	-48.1	66.3	3.63	none	36		3200
R-744 CO_2	44.01	-78.4	31.1	7.37	none	50-200	0	1

Table 1: Properties of Refrigerants [2]

)[1] molecular weight

)[2] normal boiling point at atmospheric pressure, CO_2 sublimates at this pressure

)[3] lower flammability limits are expressed in volume % in ambient air

	Unit A	Unit B	Unit C	Unit D
Refrigerant	R-502	R-502	R-507	CO_2
Charge	4.70 kg	5.20 kg	4.00 kg	1.95 kg
Compressor Displacement	233 cc	233 cc	233 cc	60 cc
Compressor Speed	1930 rpm	1660 rpm	1340 rpm	1387 rpm
Evaporator Air-Side Surface	23.76 m^2	23.76 m^2	14.87 m^2	13.28 m^2

Table 2: Technical Data of the Compared Transport Refrigeration Units

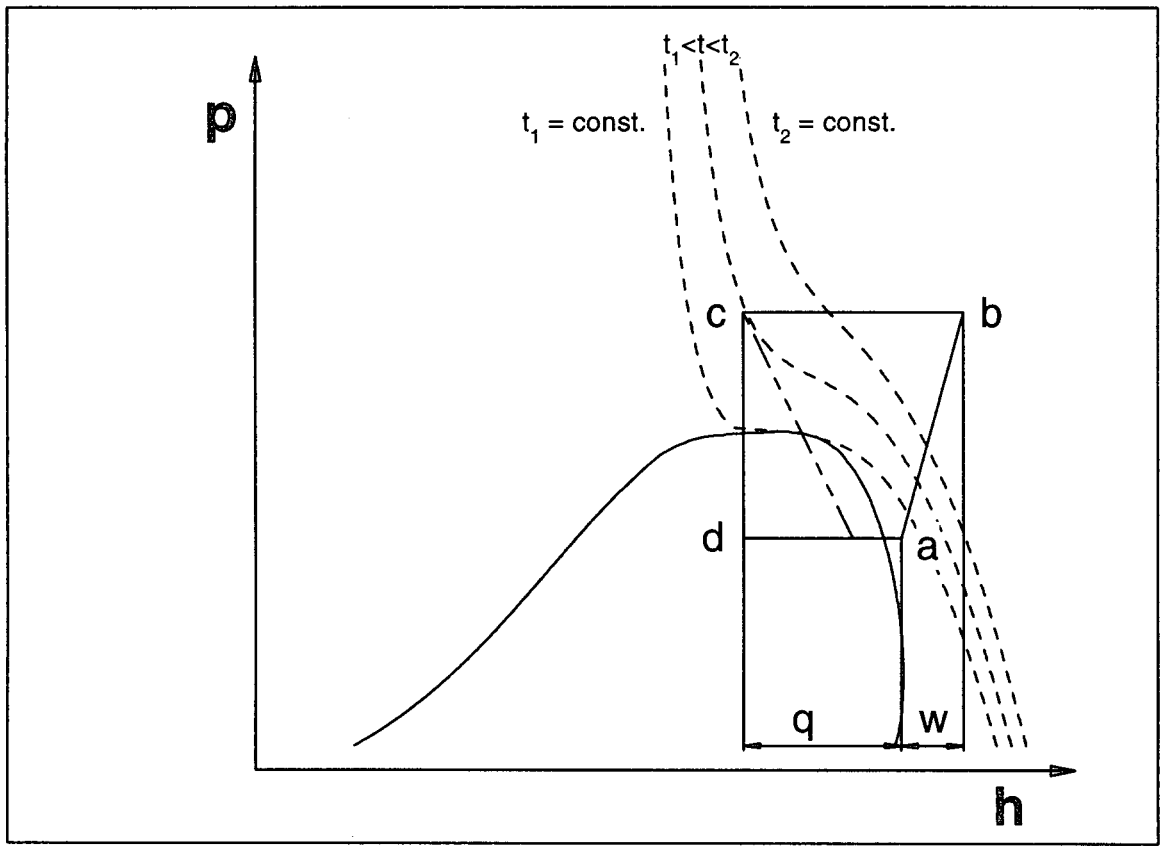

Figure 1: The Transcritical Cycle on a Pressure-Enthalpy Diagram

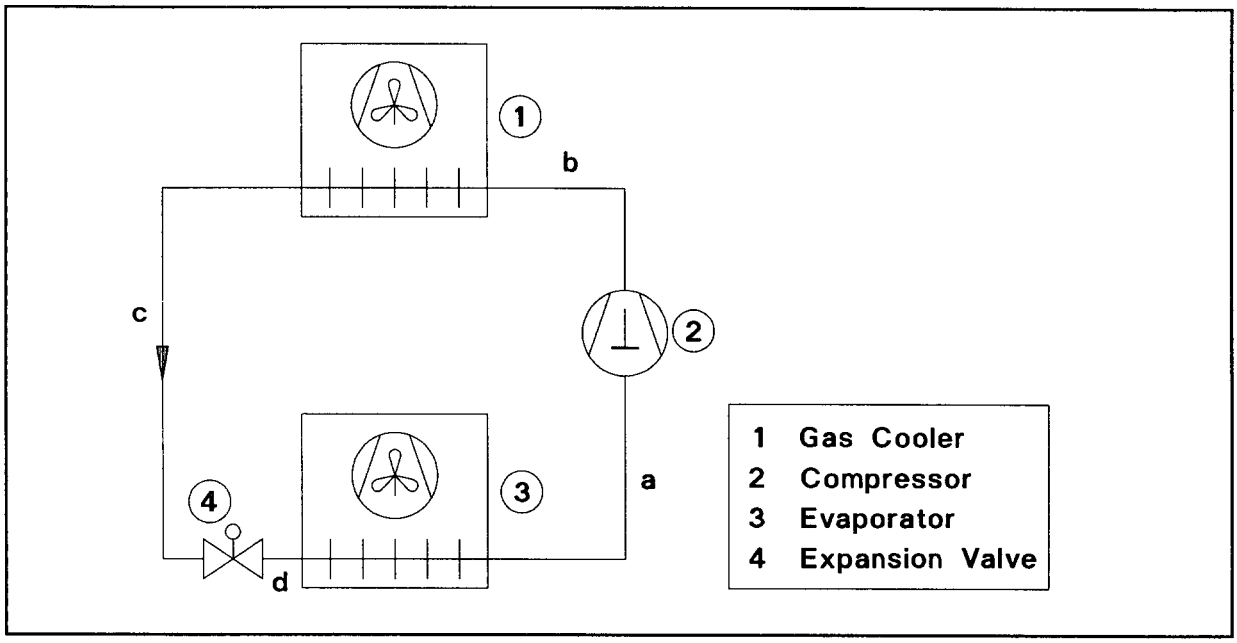

Figure 2: Refrigeration Cycle of the Present Laboratory Prototype

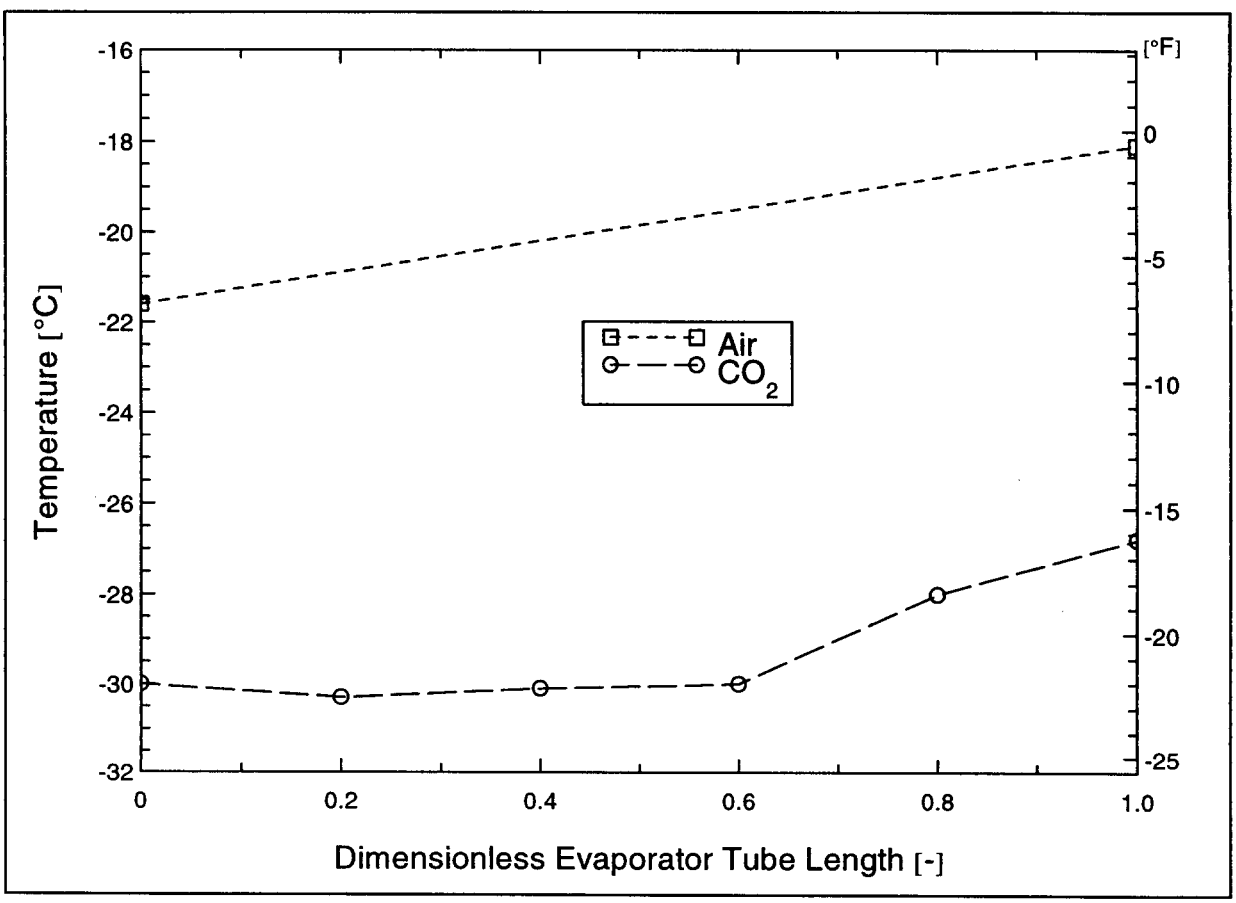

Figure 3: Temperature Distribution in the Evaporator
(Ambient Air Temperature = 30 °C / 86 °F)

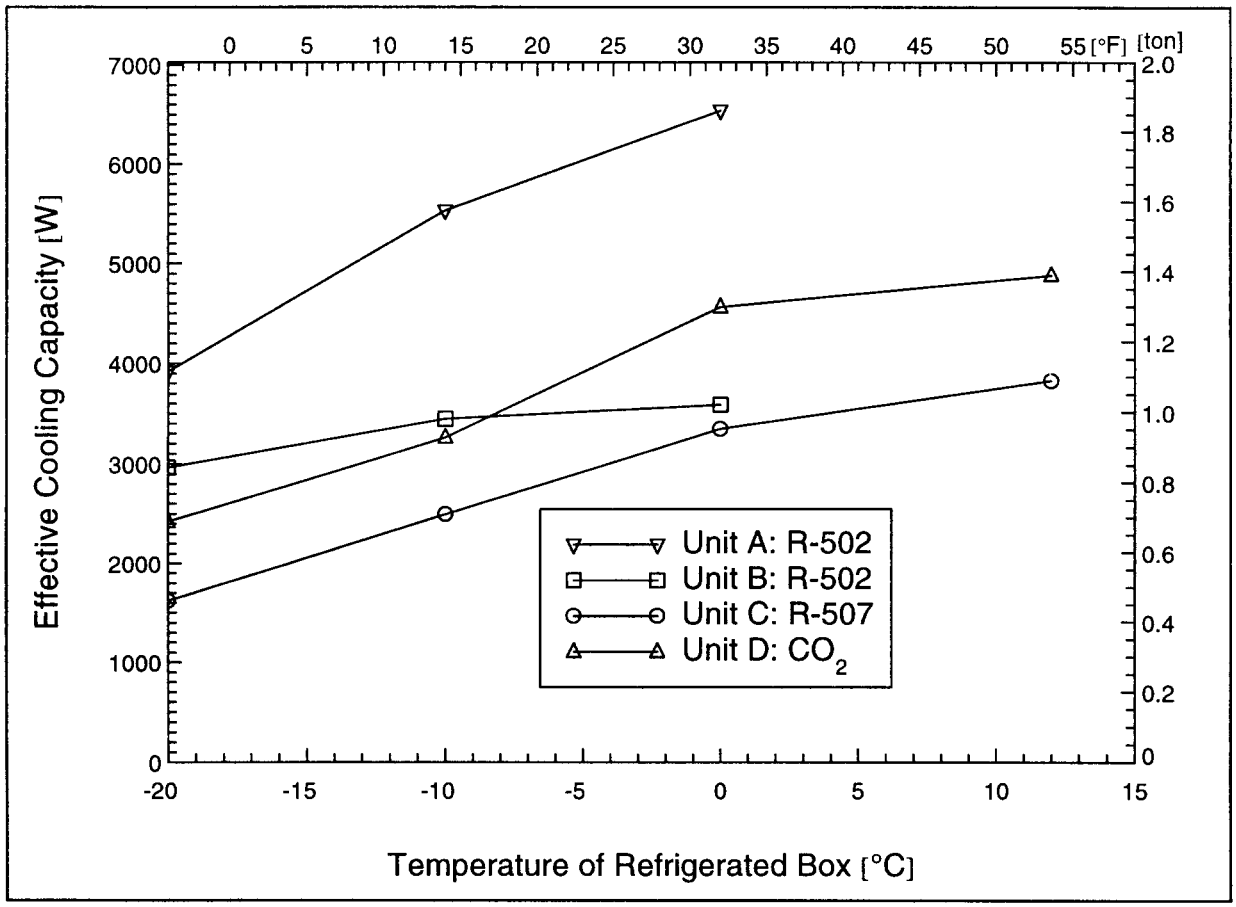

Figure 4: Effective Cooling Capacity versus Temperature of Refrigerated Box
(Ambient Air Temperature = 30 °C / 86 °F)

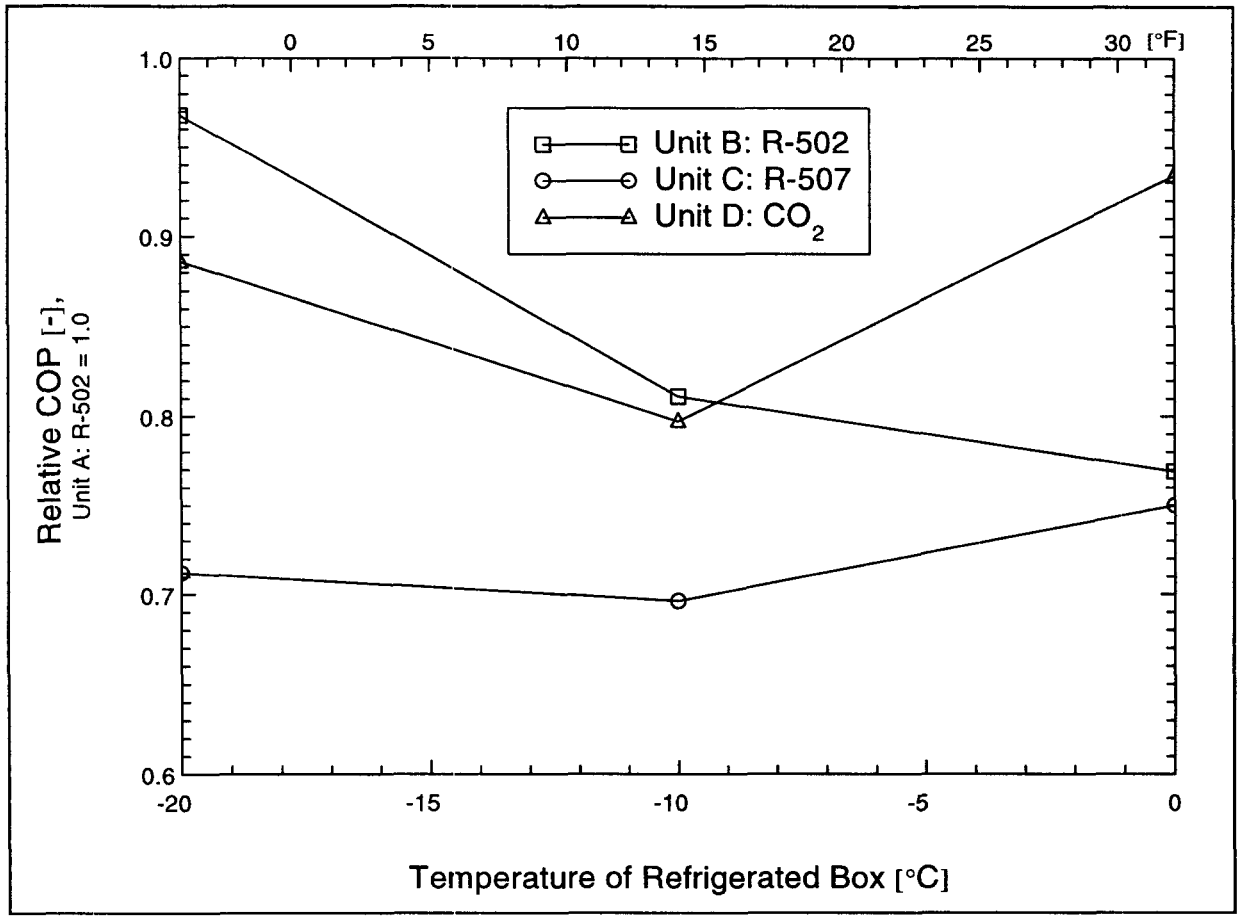

Figure 5: Relative COP (compared to the COP of Unit A) versus Temperature of Refrigerated Box.
(COP of Unit A: R-502 = 1.0, Ambient Air Temperature = 30 °C / 86 °F)

IMPLEMENTATION OF OZONE SAFE ALTERNATIVE REFRIGERANT MIXTURES IN TRANSPORT REFRIGERATION SYSTEMS: CHALLENGES AND OPPORTUNITIES

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ABSTRACT

CFC refrigerant R-502 was a popular industrial refrigerant that became widely used in low and medium temperature applications in both the transport and commercial refrigeration industries. However, the use of R-502 in new units ended December 31, 1995 due to the latest revision of the Montreal Protocol and the fact that a component of R-502, CFC refrigerant R-115, is an ozone depleting refrigerant.

There are presently four major HFC refrigerant mixtures that have been developed as long term replacements for R-502. Based on a comparative evaluation of the operational characteristics and system performance of these alternative refrigerants to R-502, Thermo King selected R-404A, a near azeotropic mixture of HFC-125, HFC-143a and HFC-134a as the best replacement for R-502. R-404A has been classified A1/A1 by ASRAE. The first AI indicates the safety classification for the mixture as formulated by the manufacturer (A is allowable exposure limit above 400 ppm, 1 is nonflammable). The second A1 refers to the safety classification of the mixture at its worst-case fractionation formulation. R-404A was formulated to meet all industry safety and performance requirements.

This paper reviews the performance requirements of transport refrigeration and the modifications made to the compressor and other components in the refrigeration system to accommodate alternative refrigerants for new unit applications. The benefits of using a new replacement refrigerant with performance characteristics very closely matched to R-502 and the benefits of the modifications made to accommodate R-404A are summarized.

INTRODUCTION

CFC refrigerant R-502 became widely used in both the transport and commercial refrigeration industries after it was introduced, especially for low and medium temperature applications. R-502 is an azeotropic mixture of R-22 (48.8%) and R-115 (51.2%) at a temperature of 66°F and exhibits a small temperature glide at all other temperatures. R-502 was originally developed to overcome the inherent high compressor discharge temperatures and lubricant return problems of R-22 at low temperature operation in refrigeration systems.

As the search for a replacement for R-502 began, no single chemical replacement refrigerant appeared to meet all of the essential criteria necessary for vapor compression refrigeration systems. Initial industry activity focused on the use of pure R-22 and its blends. R-22 is readily available world-wide and has been used in low and medium temperature applications. This made it an early candidate for use as a "transition" refrigerant to replace R-502 in transport and commercial refrigeration systems. However, R-22 has some performance disadvantages, including a higher vapor discharge temperature, and lubricant return problems in low temperature applications.

To avoid the higher compressor vapor discharge temperatures and additional system controls associated with the use of pure R-22, many refrigerant manufacturers introduced "drop-in" blends of R-22. Some of these blends have thermo physical properties similar to R-502 and can be used in transport refrigeration systems with the same lubricant. However, increasing concern over the use of a refrigerant that contains any chlorine accelerated the development of chlorine free (also called "ozone safe") HFC refrigerants and HFC blends to provide a long term solution.

Close examination of the physical, chemical and thermodynamic characteristics of pure HFC refrigerants lead to the conclusion that there is no single chemical compound candidate today that meets all the essential criteria necessary to replace R-502. However, four HFC refrigerant blends initially emerged as candidates to replace R-502 for new unit applications. During the early evaluation of these blends, the leading alternatives for R-502 were refrigerant R-404A, R-407A, R-407B and R-507. Refrigerant R-404A is classified as a near-azeotropic mixture, R-407A and R-407B are classified as zeotropic mixtures, and R-507 is classified an azeotropic mixture.

Subsequent closer evaluation of the physical, chemical and thermodynamic characteristics of these blends indicated that most of them have properties similar to R-502. Through a comparative evaluation of the operational characteristics and system performance of numerous alternative refrigerants to R-502, Thermo King found R-404A to be the best replacement for R-502 in low temperature applications on transport refrigeration systems.

TRANSPORT REFRIGERATION

Advances in technology and increases in world population have gradually made transport refrigeration an important aspect in the quality of life for many. Surveys have shown that in the twenty-first century, increasing food production to meet growing population needs will be a major challenge. Preventing food loss due to metabolic deterioration and spoilage from the growth of microorganisms will continue to increase the importance of transport refrigeration in preserving the quality of food and our quality of life.

The purpose of transport refrigeration is to maintain and control temperature to preserve product quality and extend the shelf life of commodities. Demand for the transportation of perishable or frozen commodities in refrigerated trailers, trucks or containers has increased greatly in recent years. The first source of this growth in demand has occurred because of increasing consumer demand or fresh fruits and vegetables from around the world A second source has been increasing consumer demand for horticultural products. Ornamental plants and flowers are now transported around the world. A third source has been increasing medical demand for protection of special pharmaceuticals and human organs, blood, etc. during transport. A fourth source has been increasing industrial demand for environmental control (temperature, humidity, and atmospheric gases) of special products like chemicals, photographic supplies, electronic components and special metals. A fifth source has been increasing demand for protection of art and antique products during transportation.

To achieve appropriate temperature and atmospheric conditions for transporting products, the development of effective methods of controlling temperature inside cargo compartments is very important. Unit design, refrigerant selection and operating methods are, therefore, of utmost importance to maintain accurate cargo temperature during transport.

Uniqueness of Application Requirements for Transport Refrigeration

Transport refrigeration units operate over broader temperature ranges than other refrigeration units, especially stationary unit applications (i.e. supermarket). While stationary equipment is typically installed to meet a particular load and ambient temperature requirement, transport refrigeration equipment must be capable of operating over a wide range of ambient temperatures that range from -40°F to 130°F, even while protecting product at widely different temperatures that range from -30°F to 70°F.

Under harsh, high ambient temperature operating conditions, it is especially important for unit performance that the refrigerant vapor discharge temperatures and pressures remain within safe operating limits. This is necessary to protect the refrigerants, lubricants and components in the refrigeration system. Because of these harsh operating conditions and stringent safety requirements, the number of replacement alternatives for CFC refrigerant R-502 have been particularly limited in the transport refrigeration industry.

Development and Modification of System Components for Applying HFC Blend R-404A

As the leading manufacturer of transport refrigeration equipment, Thermo King extensively reviewed and evaluated new technology for developing a reliable, long term working fluid in refrigeration systems. Comprehensive evaluations and testing focused intensely on compressors and individual components as well as the complete refrigeration system. These evaluations and practical unit tests helped contribute to the successful modification of the compressor and other individual system components to solve problems encountered during the evaluation of HFC alternative refrigerants with new lubricants.

The author recognizes that the results reported in this evaluation are dependent on the modification of the compressor and other components in the refrigeration system to accomodate the new alternative refrigerant blends and required new lubricants. Compressor modifications included new components including a new lubricant pump, new seals and a new compressor oil filter. Seals with new engineered materials and a special external oil filter were required to prevent problems such as refrigerant leaks, sludge and metal soap associated with the new polyol-ester lubricant required for HFC blends.

Evaluation of R-404A Composition Shifting

Every refrigerant blend (azeotropic, near azeotropic or zeotropic state) has a tendency to undergo a shift (segregation or fractionation) in its composition during any phase changing process (condensing or evaporating) in the refrigeration system's heat exchangers (condenser coil, evaporator coil; etc). The effect of this composition shifting is called "the temperature glide effect" and ranges from less than 1°F up to 10°F to 15°F, depending on the refrigerant blend.

Also, mixtures of vapor and liquid phase blends always coexist in components located throughout the refrigeration system. Shifts in the circulating composition of a refrigerant blend is influenced by differences in lubricant miscibility, partial miscibility and solubility with each individual refrigerant contained in a blend. The increase in flammable refrigerant concentration during leakage or composition shifting must be considered with respect to the mixture remaining non-flammable at all operating conditions. Therefore the composition changes in the blend R-404A were compared with flammability data to ensure that the concentration of flammable refrigerant R-143a remained below the flammability limits. Many laboratory and field evaluations of the blends, especially near-azeotropic mixtures, indicate that the extent of composition shifting or fractionation of compound in blends that could occur theoretically does not actually take place. These earlier evaluation results were verified by laboratory and field trial unit tests.

TEST PROGRAM

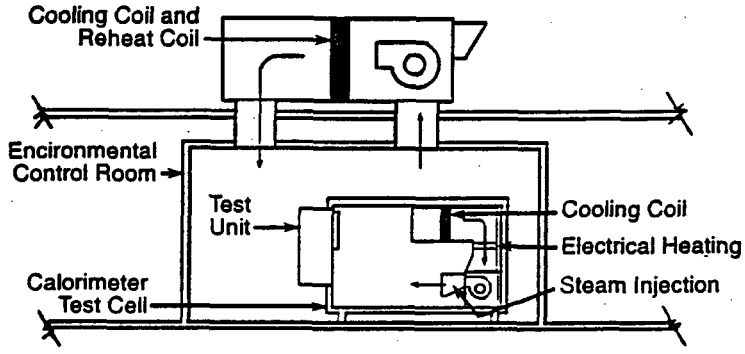
There are many theoretical cycle calculations, analytical evaluations and computer simulation results based on equations of state that can be used to identify the most promising alternatives for different R-502 applications. Also, many laboratory tests have been conducted in different research institutes located throughout the world to evaluate alternative HFC blends for R-502. However, computer simulations, analytical study and laboratory tests provide only a limited answer to the transport refrigeration industry. To determine the actual behavior of refrigerants in the compressor, components and the refrigeration system, extensive unit operating tests as well as follow-up field evaluation are necessary.

The results of our unit operating tests provided practical and realistic values for application in transport refrigeration systems. Duplicate unit tests were conducted to ensure repeatability and to verify the accuracy and reliability of all test results. Care has been taken to ensure that the data presented here is fair and comparative to each other.

Test Facilities

Test cell and calorimeter requirements were established using test standards recognized world-wide for container, trailer and truck refrigeration certification, and for bus air conditioning performance verification. The test facility has the ability to test transport refrigeration units installed on the front wall of an individual calorimeter test box. A calorimeter box is an insulated chamber where heating, cooling and humidity control equipment are installed. Heating and cooling control equipment were also installed in the room that contained the unit and colorimeter box. Figure 1 shows a typical test cell and calorimeter arrangement.

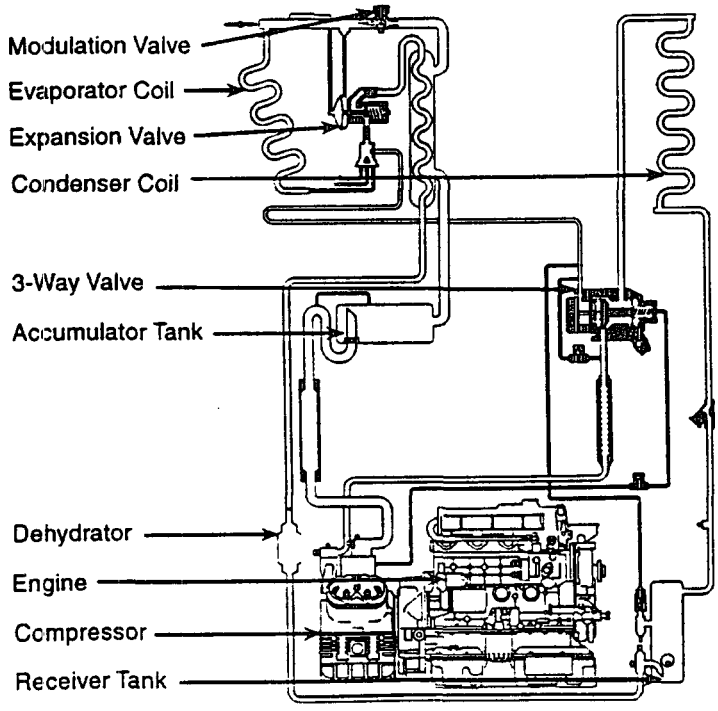
Figure 1. Typical Test Cell Section



Electric resistance air heaters were installed in the calorimeter box to provide heat during cooling tests. Cooling capacity was determined by adding the total electrical heat input to the heat loss from calorimeter box. Balancing heat load input of the electric heaters was automatically controlled using an electronically pulsing controller. A central brine chilling and liquid overfeed system is used to absorb heat loads during heating performance tests. Humidity injected in the form of dry steam was available in all test cells to test defrosting performance and add a latent heat load. Steam was introduced into the calorimeter through a steam humidifier and mixed with the air prior to entering the test unit evaporator.

Refrigeration unit coil temperature measurements were made at several locations using thermocouples soldered directly to the outside of the copper tubing and covered with foam insulation. A computer controlled data logger recorded and automatically calculated an average temperature value. Thermocouple temperature measurement accuracy is within ±1°F. All refrigeration system pressures are measured using pressure transducers connected to static pressure taps located at strategic point. Pressure transducers were calibrated to ±25% of full scale. Figure 2 shows a typical unit refrigeration system.

Figure 2. Typical Transport Refrigeration System Used in Unit Testing



Test Procedures

All tests were conducted in accordance with ARI Standard 1110-92 and applicable ASHRAE standards. Baseline tests were performed using R-502. The refrigerant and synthetic refrigerant oil charge were then removed from the system and an alternative refrigerant and POE lubricant was charged into the system. Identical oil charge levels were maintained in the system during the tests.

Lubrication oil samples were taken on a regular basis from the refrigeration system at any given set of operation conditions and analyzed to identify excessive contaminations, wear or other long term compatibility problems among the refrigerant, lubricant and components in refrigeration system

A low box temperature test was performed to test the defrosting process required to clear the evaporator coil of frost and ice.

Evaluation Test for the Impact of the Blend's Composition Change

Baseline tests with R-404A were conducted using the required unit refrigerant charge. The circulating composition of R-404A was measured during the steady state cooling performance tests. Samples were taken form the liquid line just after the receiver tank and the header tube along the evaporator coil. Sample number one was taken after one hour while the unit was in steady operation at box temperature 0°F and ambient temperature 100°F. Sample number two was taken after two hours while the unit was in stable operation at box temperature 70°F and ambient temperature 100°F. Table 1 shows the physical and environmental properties of R-404A and R-502.

Table 1: Pysical Properties of Blend R-502 and R-404A

Refrigerant Number	Composition	Molecular Weight	Bubble Point (1 ATM)	Dew Point (1 ATM)	Critical Properties			Liquid Density at 77°F LB/CUFT	Specific Heat		Density, SATD Vapor AT 5°F LB/CUFT	Vapor Pressure at 77°F PSIA
					Temp °F	Pressure PSIA	Volume CUFT/LB		Vapor 77°F & 1 ATM BTU/LB(°F)	Liquid 77°F BTU/LB(°F)		
R-502	R-22 (48.8%) R-115 (51.2%)	111.64	-49.76°F		179.9	591.0	0.02857	75.95	0.164	0.293	1.30	168
R-404A	R-125 (44%) R-143a (52%) R-134a (4%)	97.6	-50.44°F	48.82°F	162.3	535.0	0.03312	65.45	0.207	0.367	1.14	182.0

After completion of the baseline tests with R-404A, composition performance tests were conducted. The in order to change the composition of the blend different than R-404A took out a certain amount of liquid phase refrigerant from test unit and charged the exact same amount of blend R-507 for balance to get the desired composition. Same procedures for charging were repeated many times until to reach the composition of blend to blend R-507.

The only unit power source is the engine which is connected directly to the compressor. The engine drives the compressor and the blowers for the evaporator, condenser and radiator coils. Because of this power supply arrangement, the energy efficiency of replacement refrigerant blends is based on total unit fuel consumption.

TEST RESULTS

Table 2 shows the results of shifting phenomena of R-404A composition during unit operation. The refrigerant samples were drawn during unit operation from the liquid phase.

Table 3 presents shifting phenomena of R-404A composition during unit operation. The refrigerant samples were drawn during unit operation under different refrigeration load temperatures from the vapor phase.

The liquid and vapor phase samples were analyzed using a DERKIN-ELMER SIGMA 10 GAS CHROMATOGRAPH equipped with hot wire detector and a gas sampling valve. The accuracy of composition analysis in vapor and liquid phase is within ±0.1%.

The sample analysis show that there was very little difference I the specified blend composition between the liquid and vapor phases. The R-134a apparently has a lower vapor pressure amongst the three components (R-134A, R-143a and R-125), thus showing a much lower concentration in the vapor phase. Overall test results show that there were no significant fractionation with the blend R-404A.

Figure 3 summarizes the comparison data of test results over a wide range of operating conditions between the baseline refrigerant R-502 and HFC blend R-404A. Test results show that the discharge vapor pressure for R-404A was higher than R-502. However, the compressor discharge vapor temperature for R-404A was found to be much lower than for R-502. Clearly, R-404A provides good thermal stability for the lubricant as well as the refrigerant during system operation. In addition, R-404A cooling capacity and energy efficiency clearly shows a close match to R-502.

Figure 4 summarizes the unit performance results for the effect of changing the composition of R-404A by reducing the R-134a content from 4% to 0%. Test results show that the shifting of R-134a content from 4% to 0% did not have an impact on system performance.

Table 2: Shifting Phenomena of R-404A Composition In Refrigeration System During Operation

By Liquid Phase Charge

Blend R-404A			Sample 1			Sample 2			Blend R-404A Nominal Composition Range of Formulated Mixture (Liquid Phase) (Weight %)	
Refrigerant	Normal Boiling Point (°C)	Normal Composition (Weight %)	Liquid Sample Composition (Weight %)	Vapor Sample Composition (Weight %)	Difference Between Liquid and Vapor (%)	Liquid Sample Composition (Weight %)	Vapor Sample Composition (Weight %)	Difference Between Liquid and Vapor (%)	Upper	Lower
R-125	-56°F (-48.9°C)	44	44.22	45.97	+1.75	43.76	45.58	+1.82	45	43
R-143a	-53°F (-47.2°C)	52	51.9	51.61	-0.29	52.16	51.85	-0.31	53	50
R-134a	-15°F (-26.1°C)	4	3.88	2.42	-1.46	4.06	2.57	-1.51	5	3

R-404A: Boiling Point; -51.6°F & Critical Point; 162.9°F

Table 3: Shifting Phenomena of R-404A Composition In Refrigeration System During Operation

By Vapor Phase Charge

Blend R-404A			Operating Characteristics								Blend R-404A Nominal Composition Range of Formulated Mixture (Liquid Phase) (Weight%	
Refrigeran	Normal Boiling Point (°C)	Nominal Composition (Weight %)	-20°F/100°F		0°F/100°F		35°F/100°F		70°F/100°F			
			Liquid Sample Weight %	Vapor Sample Weight %	Liquid Sample Weight %	Vapor Sample Weight %	Liquid Sample Weight %	Vapor Sample Weight %	Liquid Sample Weight %	Vapor Sample Weight %	Upper	Lower
R-125	-56°F (-48.9°C)	44	43.68	44.55	44.83	43.00	44.45	43.14	44.67	43.30	45	43
R-143a	-53°F (-47.2°C)	52	53.05	52.78	52.81	52.40	52.78	52.81	52.63	52.70	53	50
R-134a	-15°F (-26.1°C)	4	3.27	3.67	2.36	4.60	2.77	4.05	2.69	4.01	5	3

R-404A: Boiling Point; -51.6°F & Critical Point; 162.9°F

CONCLUSIONS

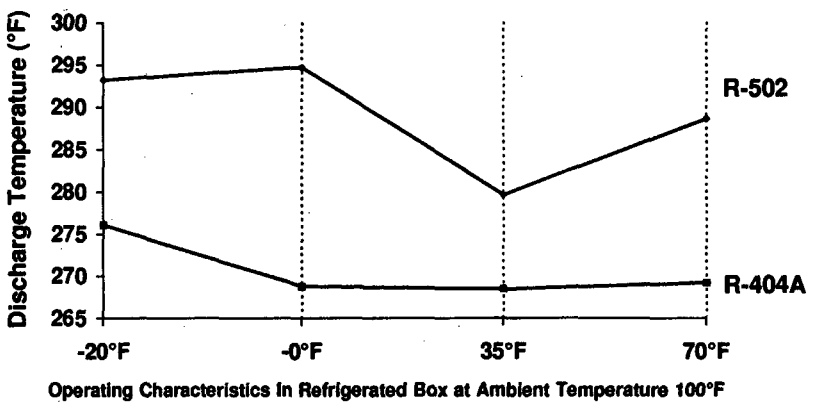
Evaluation of all laboratory and intensive field test results of several HFC alternative refrigerants indicates that R-404A demonstrates a close match to the performance of refrigerant R-502 both theoretically and in actual equipment applications. Also, R-404A provides a significant reduction in compressor vapor discharge temperatures compared with R-502 because R-404A has a greater vapor heat capacity than R-502 laboratory. Field tests demonstrated that transport refrigeration units designed to use R-502 were able to achieve essentially the same refrigeration performance with R-404A with little or no system modification.

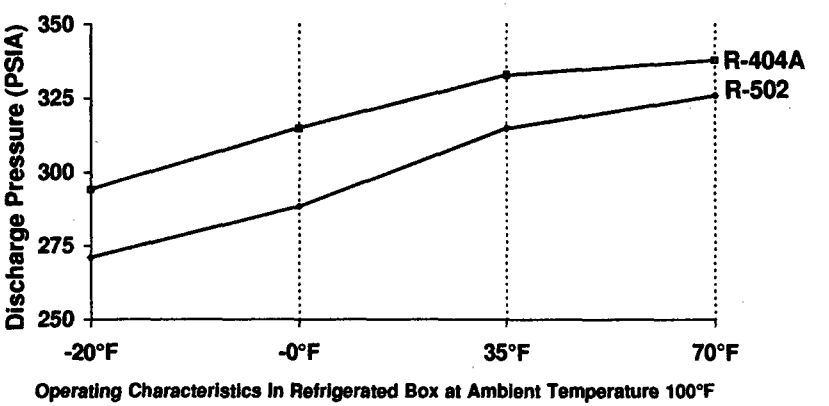
Since successfully introducing ozone safe alternative refrigerant mixture R-404A into full production in 1996, practical operation of units with modified and redesigned components has demonstrated that the application of advanced technology in engineered materials and component design can overcome many of the problems created by high discharge pressure of the new blend, material compatibility with new blend and the properties of new polyol-ester lubricants.

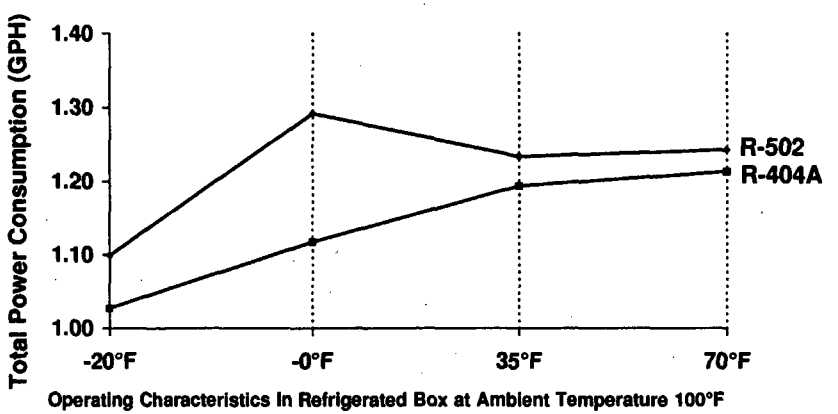
Evaluation of laboratory test results also indicate that modifying the design of the heat exchangers and other components can produce improvements in the cooling and heating performance and energy efficiency of most system's operation.

Finally, the vivid physical characteristics of R-404A revealed through the rigorous evaluation process show that R-404A proved to be the superior ozone safe replacement refrigerant for CFC refrigerant R-502 in performance if modifications to component and refrigeration system design are adequately optimized.

Figure 3. Summary of Unit Performance Test (Comparison Between R-404A And R-502)







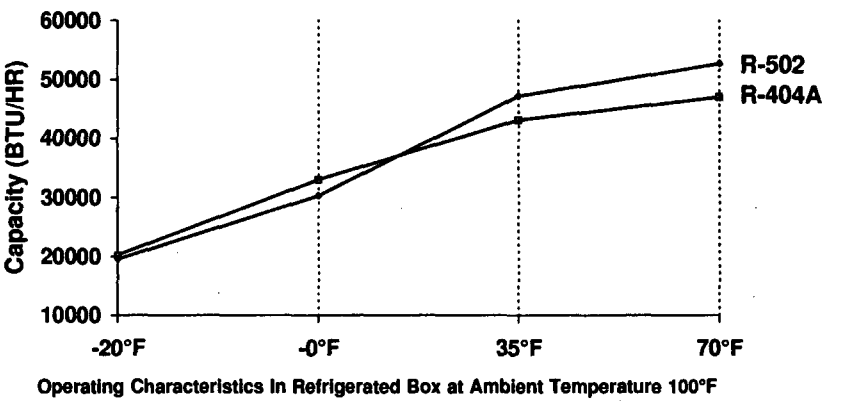
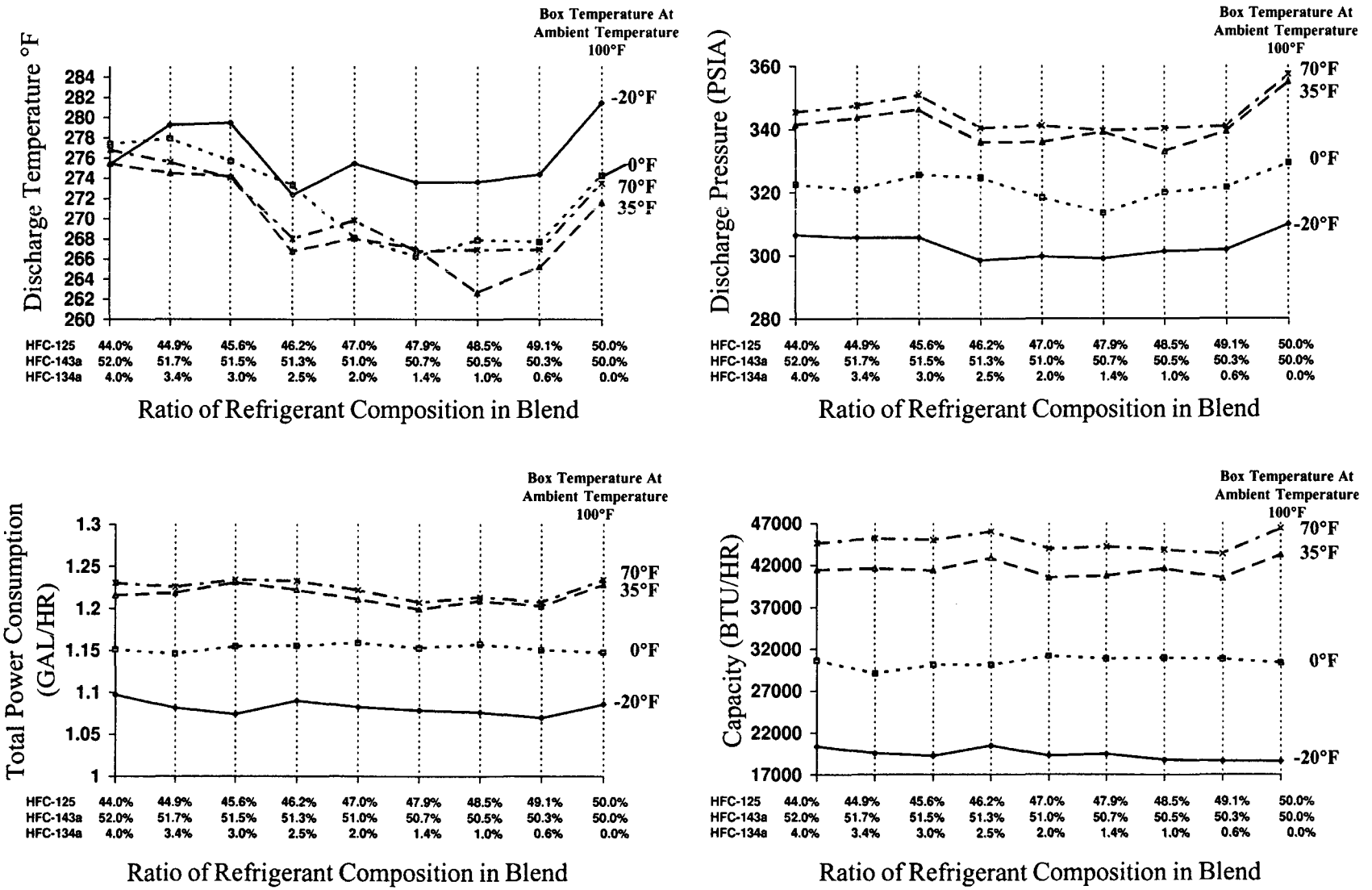


Figure 4. Summary of Unit Test for HFC Ternary Blend (Effects of Changing the Ratio of Composition)Operation: High Speed



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- FIELD TESTS USING R-404A IN LARGE SYSTEMS -

1) BACKGROUND

To face the challenge of the CFCs (ChloroFluoroCarbons) production ban in Europe the 01/01/1995, (01/01/1996 in the United States of America and in Article 2 countries), Elf Atochem has developed a comprehensive range of substitutes. The aim was to ease, regarding technical and financial issues, the CFC phase-out in compliance with the Montreal Protocol requirements and its amendments.

Today, two major long term HFC (HydroFluoroCarbons) type refrigerants have been chosen to replace CFCs in new installations for all applications : **R-134a** & **R-404A** to replace R-12 & R-502 respectively. Also, R-407C, blend of HFC-32, HFC-125 & HFC-134a has been identified and used already to replace HCFC-22 for air-conditioning applications to face up-coming HCFC regulations in some European countries.

Particularly, **R-404A**, [blend of (HFC-125, 134a, 143a @ 44, 4, 52 % in weight] is now a recognized and approved world-wide as a standard by all leading OEMs and compressors manufacturers. R-404A is intended to be used mainly in all refrigeration applications with no technical constraint. R-404A can be applied in a range of evaporating temperature as wide as [from -45°C (-49 F) up to +10 °C (+50F)] overlapping then that of R-502 it replaced initially.

Due its excellence in performance and its easiness to handle, the use of R-404A is now widespread for instance all over Europe and in United States of America. The quick success of R-404A drives now its development in the entire world. R-404A is not only used for traditional R-502 applications but also, since early 1997, for air conditioning (water-cooled chillers), in harmony with technological evolution such as scroll and screw compressors, plate-type evaporators, electronical regulation devices etc..

Of course, like all refrigerants proposed by Elf Atochem, R-404A complies with all safety criteria in terms of non toxicity and non flammability (*Underwriter Laboratories* approved) allowing therefore an easy and efficient manipulation of this fluid at minimal cost for all contractors and others professional involved in the refrigeration market

This article intends to describe several "case studies" using R-404A: Industrial refrigeration (Warehouse), process cooling in a chemical plant and climate chamber cases. All these installations running now several months or years with high expected performance.

2) R-404A IN SMALL AND MEDIUM SYSTEMS

• *Commercial refrigeration*

All major Supermarket chains have chosen R-404A for low and medium evaporating temperature applications. For instance in Europe, most of United Kingdom chains, in France (Carrefour, Casino, Auchan etc.), in Belgium (GB, Delhaize etc.), in Switzerland (Migros etc.), in Germany (Rewe etc.), in Spain (Makro, Al Campo etc.), in Finland (Kesko) or in Italy (Misa or Auchan). In the USA, Safeway, Giant Food are only examples, in South Africa (OK Bazars etc.) or in Brazil (Carrefour etc.).

• *Transport refrigeration*

Major OEMs have already adopted R-404A upon application such as Thermoking Corporation or Carrier Transicold etc., and that is on effect world-wide.

3) R-404A IN LARGE SYSTEMS : "CASE STUDIES"

3.1 Industrial Refrigeration

Many experiences have been carried out to better confirmed the excellence of performance of R-404A, in the most critical technology designs. Hereafter one example of a characteristic realisation :

"CASE OF AN INDUSTRIAL INSTALLATION WITH R-404A IN A WAREHOUSE"
- System fitted with medium and low pressure liquid receivers -

The operation took place in France mid-1996 at *ORLY GEL company*, important distributor of frozen food for instance for commercial market. The operation has been carried out in collaboration with QUIRI REFRIGERATION, contractor specialized in industrial refrigeration, Elf Atochem S.A., supplier of R-404A via its exclusive distributor in France DEHON Service, and Elf Lubricants, supplier of the Polyolester lubricant. The system has been installed in a new warehouse facility for food storage with an intended operating temperature of -27°C. R-404A has been chosen due to its world-wide acceptance and availability associated to remarkable performances at low temperatures. Besides, HCFC-22 possibility has been put aside considering low temperature requirement.

Installation description

This is a 28.000 m3 volume capacity warehouse, -27°C inside temperature, equipped with a centralized refrigeration system running with R-404A (see figure # 1). It is important to note that the truck loading docks are kept cool with a R-134a system @ 5/6°C (A/C conditions). Also due to severe constraints in food industry, the cold link must be preserved. Then particular attention had to be paid for the global system design:

- *Compression plant:* *3 APV screw type open-compressors*

- **# 1**: HS2028 model - Input power = 263 kW, Cooling capacity = 318 kW
- **# 2 & 3**: HS2024 model - Input power = 176 kW, Cooling capacity = 211 kW
- All compressors equipped with LEROY SOMER motors
- An oil separator is installed on the vapour high pressure line (870 liters capacity)

Only compressors # 1 & 2 are running to ensure a nominal cooling capacity of 530 kW to maintain the required temperature in the warehouse (with -35°/+45°C conditions). The third is a spare one to face any mechanical or electrical problems. Also to be noticed that input power of compressor # 1 is high enough to sustain cooling demand, alone, during wintertime.

- *Liquid receivers*: 2

1: 0.83 m3 capacity - medium pressure (~ 7 bar a)
2: 6.75 m3 capacity - low pressure (~ 1.8 bar a)

The #1 tank is actually an economizer allowing cooling capacity improvement and lower consumption at full-load operation.

- *R-404A charge* : ~ **4** metric tons (8,800 lbs)
- *Lubricant* : **350 liters** per compressor - Polyolester Planetelf® ACD 46 model -
- *Evaporators*: **8** fed by R-404A, liquid phase, coming from the low pressure receiver.
- *Condensers*: **3** "HELPMANN" **Air-cooled** condensers fitted with 12 fans each, whose power are 311 kW, 211 & 211 kW respectively.
- *Pipes* : Stainless steel

After compression and condensation, R-404A is injected liquid phase in the medium pressure receiver before being injected, after a second expansion, into the low pressure receiver. Then, R-404A feeds eight evaporators located in the warehouse, whose liquid transfer is ensured by pump. After circulation throughout heat exchangers, R-404A comes back into the low pressure receiver in vapour & liquid phase. The vapour of R-404A are sucked by the compressor plant from the low pressure tank. Besides, R-404A vapour phase from the medium pressure tank, is injected into the compressor : this tank plays its role of economizer.

Performance Monitoring

To assess the good operating conditions, installation parameters were recorded by computer driven dataloggers. Suction temperatures & pressures of R-404A, lubricant temperature, instantaneous input power at compressors, air-off temperatures on evaporator and condenser. Also monitoring were done overnight. As a matter a fact the installation is stopped during the day for energy cost savings concerns. In this configuration, condensing temperature can stay low. Therefore, the installation runs from 8:00 p.m. to 7:00 am until cooling duty is achieved (inside temperature of -27°C).

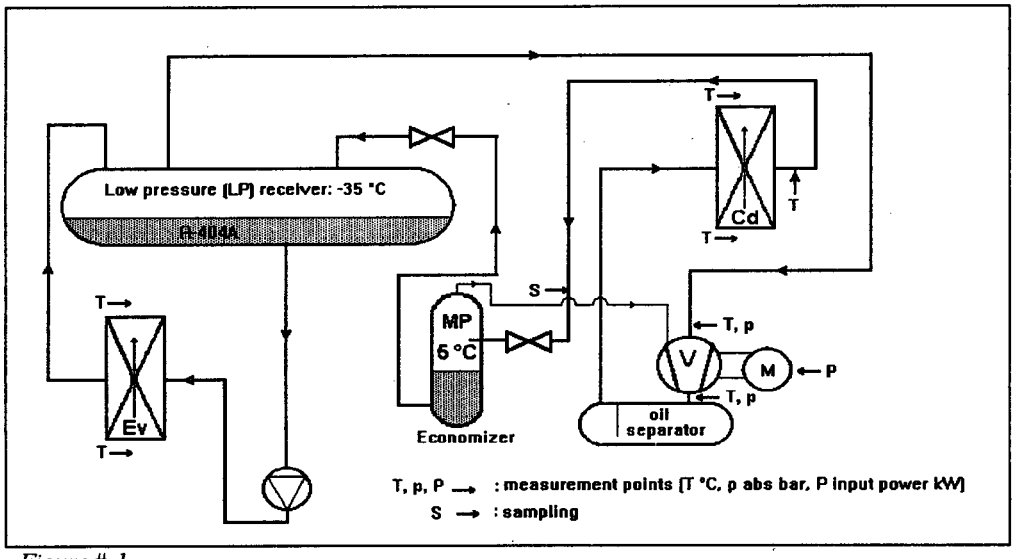


Figure # 1

During measurements, the compressor ran continuously from 20h25 to 7h00 am. Temperature data @ compressor show that outside air temperature slightly increased overnight, from 3 up to 8°C, phenomena found back on certain operating parameters.

⇨ On the following chart, pressure & temperature at suction and discharge ports of compressor are displayed. Getting over pressure drops, we can deduce a -33/+35.5°C cycle for evaporating and condensing fluid temperatures (see further figure # 2). ▫ **Active input power at compressor is about 271 kW.**

⇨ Air-off and condenser outlet refrigerant temperature sway significantly upon on/off mode. They went slightly back-up overnight with outside air temperature.

<u>Example of condenser recorded data (~2h30 am)</u>

Fan off	**Fan partially on**
Air-in T° = 6°C	Air-in T° = 6°C
Air-off T° = 28°C	Air off T° = 12.5°C
R-404A out T° = 34°C	R-404A out T° = 14°C

⇨ The next charts (see further figure # 2 & 3) represents the in/off air temperature on the evaporators for inside warehouse temperature pull-down from -24 to -27°C. As well a description of temperature profile during hot-gas defrosting :

Figure # 2

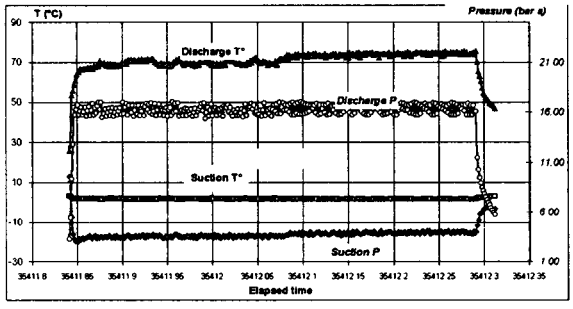
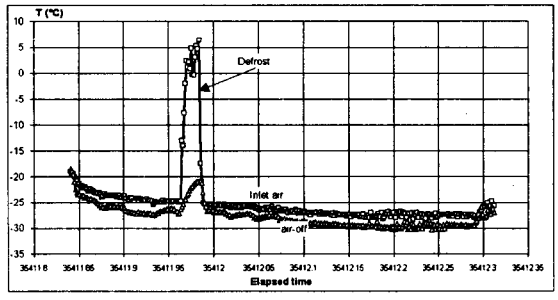
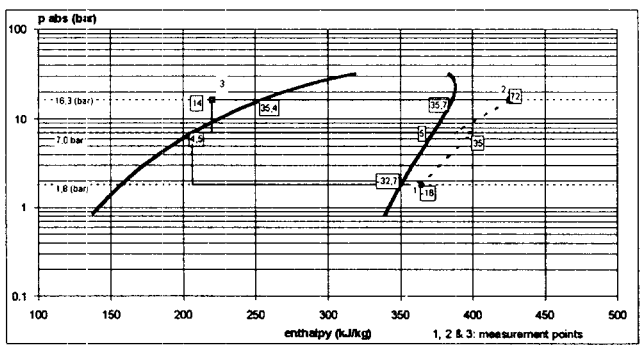


Figure # 3



⇨ The chart below does represent the real fluid cycle on a *Mollier diagram*, taking into account measured parameters (fan on & subcooling at condenser ~21°C), and assuming a 5°C temperature at economizer (intermediate compression stage @ ~7 bar a).



↳ **The cooling capacity is ~ 320 kW (calculation is based on cycle and on compressor flowrate)**
↳ **The energetic output is then close to 1.2.**

Control and analysis

In such system configuration, it was important to check the R-404A blend behaviour. As a matter a fact this configuration is very close to that of system fitted with flooded evaporator. Then, composition analysis of R-404A, near-azeotropic blend of (R-125, R-134a, 143a @ 44, 4, 52% in weight -nominal-), was made. Samples have been taken at the high pressure liquid line. Results obtained by gas chromatography, show a variation less than 2% on each component, therefore within commercial specifications.

➔ It means so that there is no composition shift and that composition of the fluid circulating at high and low pressures stages are similar. **R-404A behaves like an azeotropic blend such as R-502.**

➔ Also, the Polyolester lubricant water content was measured. We could notice an about 15 ppm decrease compared to standard specification. It is the direct result of the oversized filter drier put on the installation (contractor preferred option).

➔ Finally, metal content and acid index were found satisfying, ⇒ good running conditions of the system.

Conclusions

R-404A, as a refrigerant for industrial refrigeration applications (warehouses, ***process cooling*** etc.), for large systems (>1 metric tonne charge) fitted with low pressure receiver or flooded evaporator for example, is the suitable choice for R-502 replacement. Also, as early as today, this choice is fully in line to replace as well R-22, up to be banned in Europe the 01/01/2000 for new installations, whose input power will exceed 150 kW.

3.2 Process Cooling

Installation built a year ago and operational since 6 months for Process cooling application in Elf Atochem production facility in Calvert City, KY, USA. Installation is as follows :

- 2 "*Frick*" screw compressors (booster & primary)
- 4 remote flooded evaporators (@ -4.5, -34.5 x 2 and - 42.2 °C evaporation temperatures)
- ~ 6. 8 metric tons of R-404A (~ 15,000 lbs)

In this case, among other reasons, R-404A was the chosen refrigerant due to various operating temperature requirement : **from -45°C up to -4.5°C**. Again the high flexibility of the refrigerant is compulsory, i.e., that of R-404A. In this application R-404A, behaving like an azeotrope mixture allows the use of flooded evaporators, very commonly used in such application.

3.3 Refrigeration & A/C application : "Case of an temperature controlled chamber" :

- Retrofitting an Industrial R-502 installation to R-404A -

The retrofit took place in March 1997 at *EDF Research Center* of Renardières near Paris, France (*"Electricité De France"* - the French national electrical supply company -) of an installation which intends to control the temperature of a chamber used to test various material behaviours upon temperature changes. Climate variations can be simulated in order to reproduce outside real weather conditions where materials will be used. Any material put on the field must pass harsh temperature tests imposed by norms, standards etc.

EDF company chose to retrofit the installation with an ODP zero (Ozone Depletion Potential = 0) solution, complying with final goal of Montreal Protocol. Thus, R-404A to retrofit the "Climate Chamber" running with R-502. R-404A was chosen due to its world-wide standardisation and approval from major OEMs. The operation has been carried out in collaboration with *EDF company*, its technical service team of the Engineering Electrical R&D center, *Elf Atochem SA* via its French exclusive distributor *DEHON Service*.

The reconversion of the cooling system required then the removal of the existing lubricant from the installation running with R-502 (AlkylBenzene type lubricant). AlkylBenzene (AB) oil is not compatible (miscibility) with R-404A and was to be replaced by a Polyolester (POE) type lubricant. Following strict procedures, the AB oil was removed over a certain period of time (several flushes), without stopping the installation. When acceptable residue amount of AB oil in POE was reached (<5%), the R-502 was recovered (to be recycled later on) and R-404A refrigerant was then charged in.

Installation description : (see drawings - figure # 4)

- ❑ **1470 m³ test chamber** global volume (15 meters height x 7 meters width x 14 meters length)
- ❑ 1800 m³ total volume (chamber + evaporator room)
- ❑ Temperature operating range of chamber : from -40°C up to +60°C ($\Delta T°$ = 5°C/hour)
- ❑ Air Flowrate : 140,000 m³ /hour
- ❑ 552 kW Installed Cooling Capacity for -25°C/ +35°C conditions
- ❑ Heating power of ~ 145 kW

Compressor plant :

- ❑ 4 "Grasso" reciprocating open compressors (# RC411 model)
- ❑ 135 kW cooling capacity (-25 / + 35°C)
- ❑ Each compressor fitted with LEROY SOMER motor (110 kW input power)

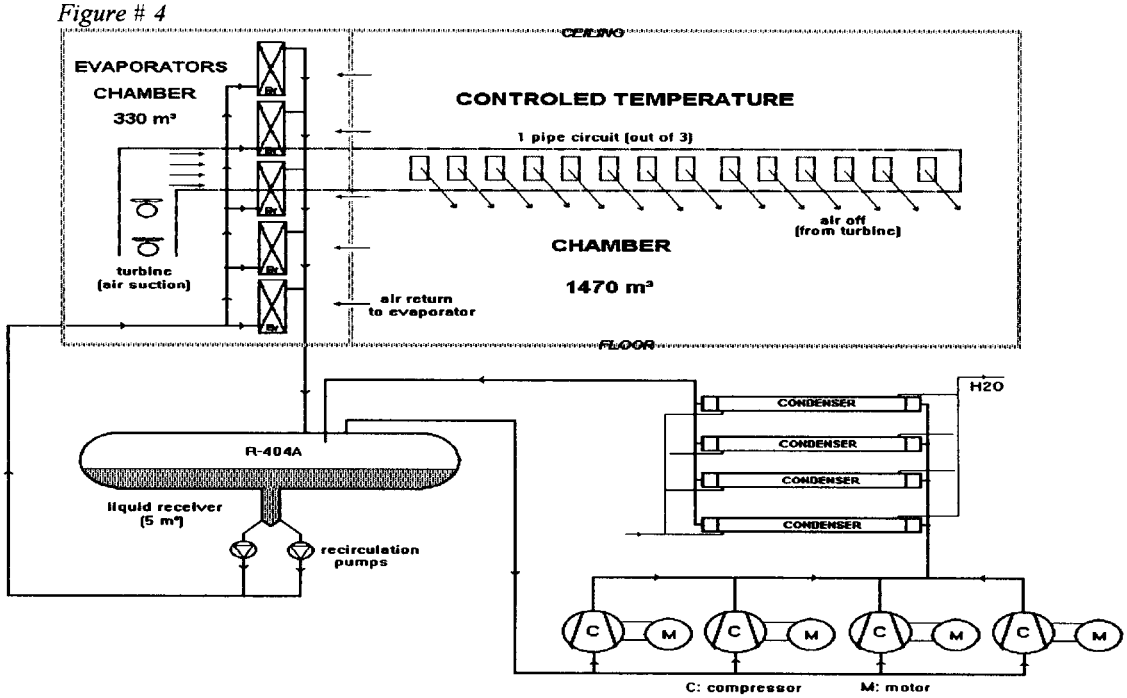
Heat exchangers & receiver :

- 4 "FRIGABOHN" Water-cooled condensers
- 5 "CONTARDO" Evaporators (total exchange surface of 392 m^2 per unit)
- 1 x $5m^3$ Low pressure liquid receiver

Fluid and lubricant :

- 2,200 kilos (~4,840 Lbs) of R-404A
- MOBIL EAL Artic 68 Polyolester oil : 22 liters per compressor

Figure # 4



Way of operation :

- The compressor plant sucks R-404A, vapour phase from the low pressure liquid receiver.
- R-404A after compression is condensed and then goes back to the receiver.
- From liquid receiver, two pumps transfer R-404A, liquid phase, into the evaporators where it will expand to cool the air inside the chamber. To note that air flow is ensured by two turbines which sucks air from the chamber and blow it after it went through evaporators.
- Two or three compressors are sufficient to fulfil the cooling duty. The fourth one is a spare one.

Monitoring :

In order to assess the success of the operation, different parameters were recorded with computer driven devices (dataloggers etc.) comparing R-502 before retrofit and R-404A. Results are displayed in the following tables:

PARAMETERS : PRESSURES-TEMPERATURES							
		Step down to 0°C (70 to 130 min)			Step down to -20 °C (R-502 265 to 300 min, R404A 225 to 264 min)		
		R-502	R-404A	Variation	R-502	R-404A	Variation
COMPRESSOR							
Suction T°	°C	-13	-14	*-1 K*	-25	-27	*-2 K*
Discharge T°	°C	58	46	*-12 K*	65	52	*-13 K*
Suction pressure	bar a	3.3	3.5	*5%*	1.90	1.96	*3%*
Discharge pressure	bar a	14.9	13.6	*-9%*	14.4	13.4	*-7%*
CONDENSER							
Inlet température	°C	51	41	*-10 K*	57	48	*-9 K*
Outlet temperature	°C	32	25	*-7 K*	33	26	*-7 K*
Temperature difference	K	*19*	*16*		*24*	*22*	
Outlet water temperature	°C	26	22	*-4 K*	25	22	*-3 K*
TemperatureDifference	K	*15*	*4*		*14*	*3*	
EVAPORATOR							
Inlet temperature	°C	-13	-14	*-1 K*	-29	-29	*0 K*
outlet temperature	°C	-13	-13	*0 K*	-29	-29	*0 K*
variation	K	*0*	*1*		*0*	*0*	
Air-in temperature	°C	2	1	*-1 K*	-19	-19	*0 K*
Air-off temperature	°C	-8	-8	*0 K*	-26	-26	*0 K*
Difference	K	*10*	*9*		*7*	*7*	

ELECTRICAL PARAMETERS							
Input power	kW	86.5	86.9	0.5%	60.4	59.8	-1.0%
Tension	V	393	391	-0.5%	391	387	-1.0%
Intensity	A	163.50	164.10	0.4%	125.50	124.2	-1.0%
Consumption (1)	kWh	86.61	86.79	0.2%	35.19	35.18	-0.03%

(1) Measured over a 60 minutes period for the 0 °C step and 35 minutes the -20 °C step

Calculated values							
		Step 0°C			Step -20 °C		
		R-502	R-404A	*VARIATION*	R-502	R-404A	*VARIATION*
Evaporator inlet T°(1)	°C	-16.5	-16.3		-31.0	-31.4	
Evaporator outlet T° (2)	°C	-16.5	-15.7		-31.0	-30.7	
Average T° of evaporation	°C	-16.5	-16.0		-31.0	-31.1	
Inlet / outlet T° @ condenser (3)	°C	35.0	28,2/28,6		33.6	27,7/28,0	
Average T° of condensation	°C	*35.0*	*28.4*		*33.6*	*27.9*	
Superheat	°C	*3.5*	*2.3*		*6.0*	*4.4*	
Compression ratio		4.49	3.91	*-13%*	7.58	6.84	*-10%*
Volumetric compression work	kJ/m³	722	688		556	534	
COP		2.59	3.12	*20%*	1.81	2.09	*16%*
Volumetric cooling capacity	kJ/m³	1872	2306	*23%*	1005	1116	*11%*
Isentropic output		71%	70%		74%	74%	
Cooling capacity: calculation based on refrigeration cycle							
Compressor volumetric output (4)		0.78	0.80		0.62	0.66	
Nominal flowrate (5)	m³/h	531	531		531	531	
Effective flowrate	m³/h	412	427		330	349	
Cooling capacity (6)	kW	214	274		92	108	
Cooling capacity: based on electrical consumption							
Input power @ compressor	kW	86.5	86.9		60.4	59.8	
Motor output (estimation)		0.9	0.9		0.9	0.9	
Cooling capacity (7)	kW	202	244		98	112	

(1) Calculated with enthalpy of measured point @ condenser outlet (2) For R-404A, the value is the dew T° @ suction pressure
(3) Calculation based on discharge pressure (4) Volumetric compressor output =1 - 0.05 x compression ratio
(5) For 4 cylinders, based on 132,7 m³/cylinder (6) Cooling capacity=effective flowrate x volumetric cooling capa/3600
(7) Cooling capacity = COP x input power @ compressor x motor output

Result comments :

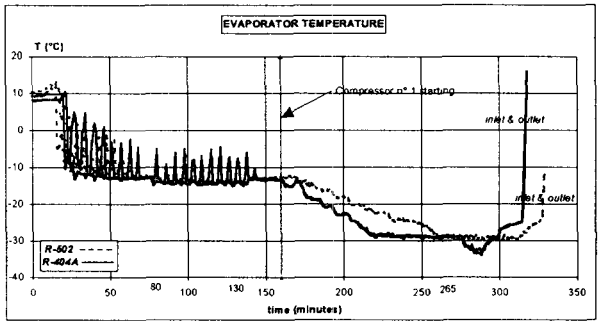
➔ Experimental data :

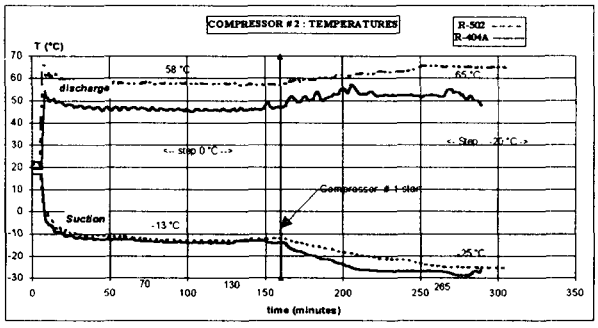
- They show that R-404A exhibits quite lower discharge temperature & pressure in all cases (To reach 0°C & -20°C inside chamber temperature),
- Over the same period of time, electrical consumption is equivalent for both R-502 & R-404A to reach the same inside chamber temperatures (0 & -20°C).

➔ Thermodynamical assessment on compression cycle of experimental measurements show as well the excellent performance of R-404A vs. R-502 :

- Lower compression ratio (~10% average upon temperatures)
- Lower temperatures @ condenser
- Higher volumetric cooling capacity (from 11 to 23 % increase)
- Better COP (16 to 20 %)
- Higher refrigerating capacity at similar flowrate (based on cycle & electrical consumption)

Example of running parameter recordings :





To sum up with all the results, we can consider that performance obtained with this refrigerant are even better than that of R-502, as behaviour and manipulation of both fluids are the same The installation is running well and global post-retrofit technical follow-up confirm the good operating parameters.

Conclusions :

R-404A showed in this case that it is a very suitable solution for this kind of application. R-404A proves its high flexibility for an application requiring to work in a wide range of evaporation temperature (from -45° up to +10°C]. This application can be considered as refrigeration application field when operating at low temperatures (-45 to -20°C) or as air-conditioning field when operating between 0 an +10°C.

GENERAL CONCLUSIONS

R-404A is now used everywhere in refrigeration applications with no technical constraint of any kind (technology, temperature range etc.) since more than three years. This success encouraged OEMs, contractors and end-users to adopt it at industrial levels. Now R-404A is widely used in industrial refrigeration with different installations configurations (DX expansion, low pressure liquid receivers, flooded evaporators with all kind of compressors etc.).

Moreover large air-conditioning systems (water cooled) are being developed, taking advantage of the HCFC-22 available technology (soft optimization). Then, we can say that R-404A does more than only replacing R-502 in its applications, but triggers application enhancements and technology evolutions to get along with user requirements : Standardisation.

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ACKNOWLEDGEMENTS

- We would like to address a special thank to ORLY GEL company and DEHON Service, for their involvement and assistance (Case of Industrial Refrigeration: Warehouse with R-404A)

- Special regards to EDF French National Company - especially to MM. BASILLE & LIMOGES* from the R & D Center of the Renardières, for their precious assistance and technical help and DEHON Service. (Case of "Retrofitting a Climate Chamber running with R-502 to R-404A").

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REFRIGERANT BLENDS - TECHNICAL CONSIDERATIONS OF RECOVERY AND RECYCLE OF REFRIGERANTS IN MOBILE AIR CONDITIONING SYSTEMS

September 1, 1997

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ABSTRACT

The USA Clean Air Act requires recovery of all replacement refrigerants including refrigerant blends. There are no specifications that identify requirements for recovery or recycle equipment for these refrigerant blends. This paper addresses potential requirements as they relate to present practices and identifies the technical considerations of recovery and recycle of refrigerant blends.

INTRODUCTION:

The Montreal Protocol, the USA Clean Air Act, and subsequent EPA regulations are intended to preserve the earth's protective ozone layer. This has had an impact on the mobile air conditioning system market, from automobile manufacturers to the service technicians and individual automobile owners since R-12 production has been discontinued in the USA. It is necessary to implement all possible actions to preserve usable amounts of R-12 to service existing equipment. As supplies diminish, alternatives will compete for the replacement market. New refrigerants have been developed to replace R-12 in mobile air conditioning systems and are available in the marketplace. Some of these alternatives are known as refrigerant blends. Since refrigerants are required to be recovered and the mobile air conditioning market is accustomed to recycle refrigerants, it is necessary to identify the requirements applicable to recovery and, if possible, recycling of the refrigerant blends currently approved for the mobile air conditioning market system. This is intended to assist in the development of suitable recovery or recycle equipment.

BACKGROUND:

Refrigerant 12 (R-12) was the only refrigerant traditionally used in mobile air conditioning system applications. As a result of years of experience the properties of the gas and the cooling systems are well understood. Service procedures for R-12 are well defined and, for the most part, uniform from vehicle to vehicle. Risks and hazards are well understood and integrated into the design, operational and service procedures.

When researching alternate refrigerants for new vehicles, required due to the banning of the production of R-12, one fundamental consideration was to develop an alternative that would not create significant differences in current equipment or procedures and where an equivalent level of field experience could be created and feedback developed to influence design, operation and service of future systems. The choice was made by auto manufacturers early once they understand that R-12 would be banned and when there were few possible alternative refrigerant choices. Refrigerant R-134a seemed to meet most of the fundamental criteria for an alternative. However, it was necessary to change the type of oil used, to modify some system components and to revise the system design to accommodate the slight difference of performance of R-134a. Prior to 1995 there were two possible refrigerants being used by OEM's in vehicles, R-134a and R-12. After 1995, R-12 would be available only from existing stockpiles or in recycled form and all new cars used R-134a. It was, therefore, necessary to identify the refrigerant that was in a vehicle air conditioning system and develop methods to minimize and avoid, if possible, the mixing of the two chemicals.

In order to preserve supplies of R-12 as long as possible, to service existing vehicles, it is the intent of Section 609 of the Clean Air Act to recycle R-12 used in mobile air conditioning systems.

SAE STANDARDS:

SAE Standards were developed to address system design recycle/recovery procedures and service procedures.

The basic objectives of these standards are:

1) recycle existing supplies of R-12 as long as possible and recycle R-134a in a similar manner,
2) to fully qualify any new alternate refrigerant,
3) be sure that a service technician would know what refrigerant was in the vehicle, and
4) provide design features that would help to avoid accidental mixing of different refrigerant gasses and thereby avoid putting the wrong refrigerant gas into a vehicle.

Other major points in these standards are:

1) The alternate refrigerant is to be nonflammable when tested in a 66°C ambient (Ref: Clause 5.2 of SAE Standard J1657). Fractionation shall not result in flammability of the refrigerant.
2) The refrigerant system is to be fitted with unique fittings for service hose connections when R-134a is used as the alternate. (Other alternative refrigerants have similar rules specified by the EPA.)
3) The refrigerant system is to be marked to identify that the refrigerant R-134a is used as the alternate. (Other alternate refrigerants have similar rules specified by the EPA.)
4) The toxicity of a refrigerant is covered by reference to the US EPA's Chemical Inventory list as required by the Toxic Substance Control Act (TSCA).
5) The requirements for purity of the recycled refrigerant (R-12 and R-134a) are specified.
6) The refrigerant shall be compatible with the materials used in the air conditioning system (SAEJ1662).
7) Vehicle performance tests are conducted with the retrofitted refrigerant to confirm that the system cooling capacity is equivalent to the original R-12 system.

SNAP:

SNAP (Significant New Alternative Program) is the U.S. EPA's program for evaluating alternative refrigerant. SNAP concepts for vehicle air conditioning systems, that are retrofitted with a new refrigerant, include the following:

1. The refrigerant system is to be marked to identify the refrigerant.
2. The refrigerant system is to be fitted with unique fittings for service hose connections.

The reasons for these requirements relate to Section 609 of the U.S. Clean Air Act of 1990. The requirements were developed to help avoid mixing different refrigerant gasses, particularly with R-12.

REGULATIONS:

For mobile air conditioning system service technicians, the critical points in the Clean Air Act of 1990 and subsequent EPA regulations are:

- The regulated refrigerant gasses shall not be vented to the atmosphere (i.e. CFC's and HCFC's).
- Any CFC refrigerant gasses must be recovered and shall not be vented to the atmosphere.
- The regulations support the SAE standards principles.
- Any alternate refrigerants must be accepted by the EPA under SNAP (Significant New Alternative Program), and to obtain SNAP acceptance, the following criteria is evaluated:

a) The refrigerant must be nonflammable or the risk of flammability fully qualified.
b) The health effects and the environmental impact are evaluated for compliance with the Clean Air Act by the EPA.
c) The safety aspects of the refrigerant are considered.
d) Retrofitted vehicle air conditioning systems shall be marked to identify the refrigerant.
e) The retrofitted system shall be provided with unique service fittings.
f) The refrigerant shall be recovered and could be subsequently reclaimed or recycled. It shall not be vented to the atmosphere.

SERVICE OF MOBILE AIR CONDITIONING SYSTEMS:

From the perspective of the 1996-1997 time frame, there is a need to provide service for mobile air conditioning systems that require recharge or repair and that have been designed for Refrigerant R-12. When determining how to best service these systems, the following options are available:

- Use R-12 available from stockpiled or recycled supplies or from a reclaimer.
- Install a retrofit kit developed by the vehicle manufacturer using an EPA acceptable refrigerant. Presently many, but not all, vehicles can be retrofitted by a procedure specified by the vehicle manufacturer using Refrigerant 134a.
- Use some other method not necessarily approved by the vehicle manufacturer, but is acceptable to the EPA and the customer.
- Do not repair the vehicle's air conditioning system.

Decision Tree No. 1 is based on conditions that have been reported in the mobile air conditioning system market and illustrates options with information related to each other.

SUBSTITUTES:

The EPA has "accepted" nine substitutes for vehicle air conditioning systems (as of October 1996). One of these is R-134a which is being used in all new vehicle air conditioning designs. All others are blends of different refrigerant gasses designed to replace R-12 in a mobile air conditioning system with

a minimum amount of system changes and to match, as close as possible, the characteristics of Refrigerant-12.

The following identifies characteristics of R-12 systems that are considered important to match.

- Pressure-Temperature Characteristics
- Material Compatibility Characteristics
- Refrigerant Containment System Compatibility
- Oil Compatibility

RECOVERY/RECYCLE OF MOBILE AIR CONDITIONING REFRIGERANT:

These same items are also major considerations in the ability to recover or recycle blended refrigerants that could be used in a vehicle. They affect the design of the recovery or recycle equipment and the ability of that equipment to operate safely and to provide a usable recycled refrigerant.

Decision Tree No. 2 illustrates the current options identified in the mobile air conditioning system market when a blend is to be considered for removal from a vehicle.

REFRIGERANT BLEND RECOVERY/RECYCLE:

For blends, all of the options illustrated may not be technically feasible.

Diagram 1 is a system requirement/functional diagram of a possible "universal" mobile air conditioning refrigerant blend recovery and/or recycle machine. It is expected for the purposes of this discussion that the refrigerant would be recovered first and, if recycling can occur, it would be another step after recovery.

The objective of the diagram is to identify critical parameters related to what could occur in the field and define the system requirements to address potential safety and environmental risks. When these items are understood, suitable equipment designs capable of handling the functions intended could be produced on a cost effective basis.

RECOVERY AND RECYCLE EQUIPMENT:

The most desirable piece of equipment for service would be a machine that could collect any and all refrigerants that are expected to be in a vehicle and, after separating, cleaning and properly remixing the blend, deliver a particular recycled refrigerant for return to the vehicle. The particular recycled refrigerant (blend or single component refrigerant) would be specified by the operator as the one suitable for that vehicle based on the markings and fittings. However, the technologies related to chemical identification, chemical separation and the recovery/recycle process have not advanced sufficiently to permit a cost effective solution. At this time, the most likely destination for an unknown mixture of chemicals in a recovery tank is destruction.

RECOVERY EQUIPMENT:

The most practical type of equipment would be a recovery machine that could recover any and all refrigerants that are expected to be in a vehicle and recover them into a tank

identified for leaving the service site for destruction or possible reclamation. Focus is presently on developing the initial requirements for this type of equipment. A future option would be to consider the parameters applicable to recycle equipment.

SINGLE REFRIGERANT BLEND RECOVERY EQUIPMENT:

A recovery machine would be designed to process one particular blend. In which case, it would be necessary to know that the refrigerant in the vehicle is the one that the machine is designed to recover, that the refrigerant recovered is the refrigerant intended, and that refrigerant is identified on the container or is returned to a vehicle with the proper fittings and markings.

REQUIREMENTS, RECOVERY EQUIPMENT:

In developing the requirements, the recovery equipment will need to adequately process any possible mix of refrigerants. The following are considered.

a. What design/pressure and safety factor should be applied to the pressure containing parts.
b. The equipment materials that are in contact with the refrigerants shall be compatible with all the possible chemicals.
c. The performance of the oil separator shall be specified and confirmed.
d. The fill percentage of the refrigerant containment tank shall be properly specified and limited by equipment design, to avoid the risk of a tank explosion.
e. The possible flammable aspect of the refrigerant gasses should be addressed with respect to the risk of a hazard to a service facility if flammable gasses could leak from a vehicle, the recovery equipment, or the tank and hoses.
f. The material compatibility of hoses and seals shall be specified to meet the current compatibility requirements for each refrigerant component.
g. The hoses will be permanently supplied with the equipment and one will be provided for each type of fitting associated with an "acceptable" blend. (Note: The EPA may rule on the use of adapters. Adapters are not currently permitted.)
h. There may be other items critical to system designs, usage, OEM concerns, etc.

The chemicals that could be present shall be only those known to be in vehicles today and those contained in refrigerants or refrigerant blends that have been accepted by the EPA. The oil types are those known to be used in vehicles at the present time. The moisture levels are related to the oil and refrigerant characteristics. Particulates are required to be filtered out at the same level as is presently specified for R-12 and R-134a. Air contamination is expected to be at the same level being experienced today for a specific refrigerant. The requirements for oil separation are similar to those for R-12 and R-134a, but must include oils known to be in a mobile air conditioning system.

Because several flammable substances could be present (R-290, R-600, R-600a, R-142b are classified as flammable refrigerants) the equipment shall be designed for use in Class 1, Division 2 locations. Because the equipment processes possible flammable gasses, but these gasses are not normally present in the atmosphere, the location where these machines will be used must be a suitable Class 1, Division 2 location.

The recovery tank shall be identified as a container of unknown refrigerant (colored gray with a yellow top). Because the tank is not identified and the equipment may be capable of handling any possible mixture of chemicals that may be recovered (as noted in Diagram 1), there is no need to identify by test what was in the vehicle, what is going into the recovery equipment or what comes out of the recovery equipment. The test points noted in Diagram No. 1 would not apply.

REQUIREMENTS, RECOVERY FOR SPECIFIC BLEND EQUIPMENT:

In this case, the refrigerant in the vehicle can be identified by the markings and fittings on the vehicle. The refrigerants may need to be identified by a suitable refrigerant identifier (Test Point A). It would also be necessary to identify by test that the refrigerant in the recovered tank is the refrigerant specified (Test Point B).

REQUIREMENTS, RECYCLE EQUIPMENT:

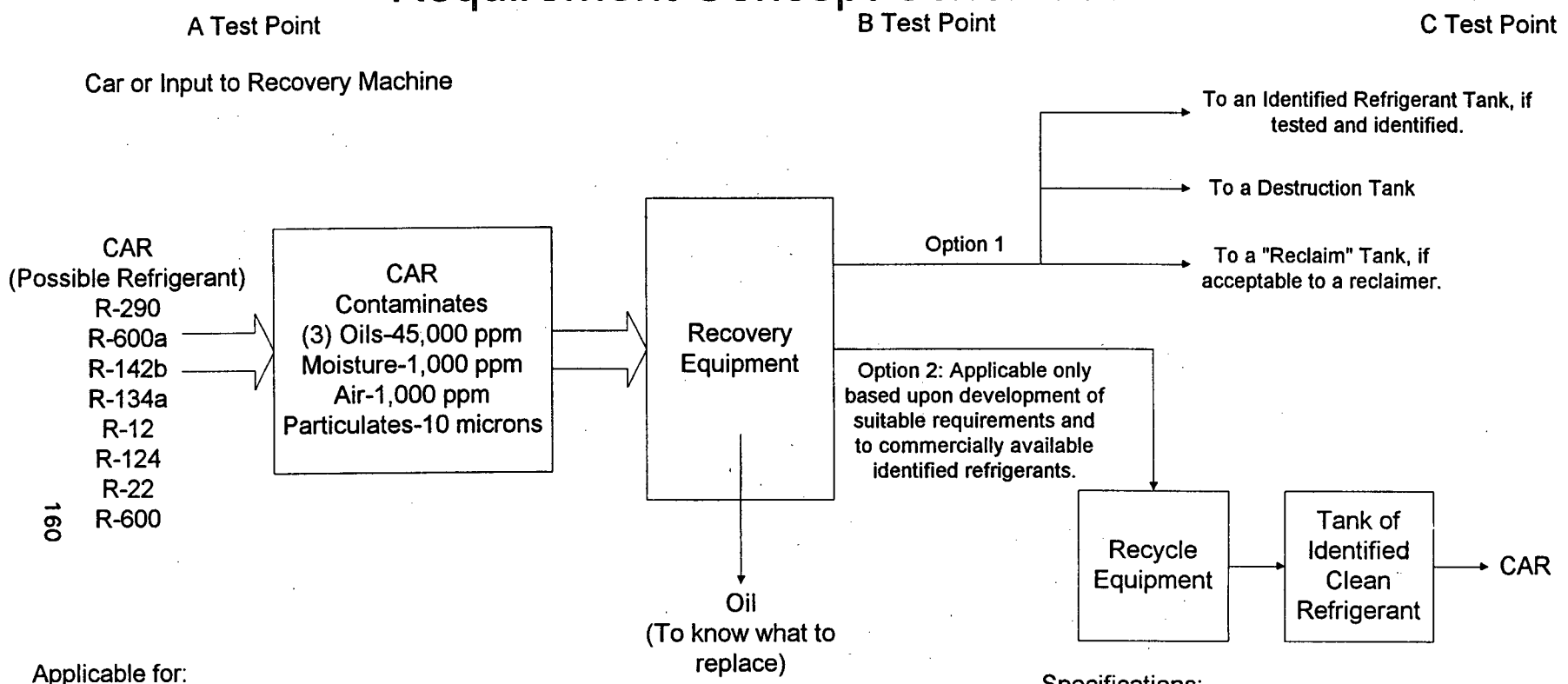
For recycle equipment, the basic function would start just before Test Point B. It may be possible to recycle a known refrigerant that is tested at Test Point B and know that the resultant refrigerant from the recycle machine is an acceptable refrigerant for use in the mobile air conditioning system. However, tests at one or the other Test Points (B or C) would be necessary to fully qualify what is returned to the vehicle.

SUMMARY:

The Montreal Protocol is intended to preserve the earth's stratospheric ozone layer, and protect the health of all the earth's occupants. The Protocol and subsequent USA legislation and regulations are intended to preserve the ozone layer and have eliminated production of R-12. To provide cost effective service for using R-12 in air conditioning systems, it is necessary to implement all actions possible to preserve the present supply of R-12 through recycling and recovery. In addition, suitable alternatives are being developed. The USA regulations require recovery of all refrigerants and most of the mobile air conditioning system service technicians are accustomed to recycling. Since these are alternative refrigerant blends available in the marketplace, it is necessary to identify the requirements applicable to recovery and/or recycling of these blends to assist manufacturers in developing suitable equipment.

The requirements for such equipment, along with the technical rationale, and the present status of the market have been identified.

Diagram No. 1
Requirement Concept Schematic



Applicable for:
Components of "accepted" EPA blends and only chemicals known to be in mobile air conditioner system.

High contaminate levels that could be in the refrigerant and in the system.

(3) Oils
Mineral Oil
Polyalkylene glycol (PAG) Oil
Polyol ester (POE) Oil

Specifications:
_% of identified blend components
___ oil
___ moisture
___ air
___ particulates
(to be developed)

EPA "ACCEPTED" blend refrigerant, also accepted by equipment owner, service facility or other responsible organization.

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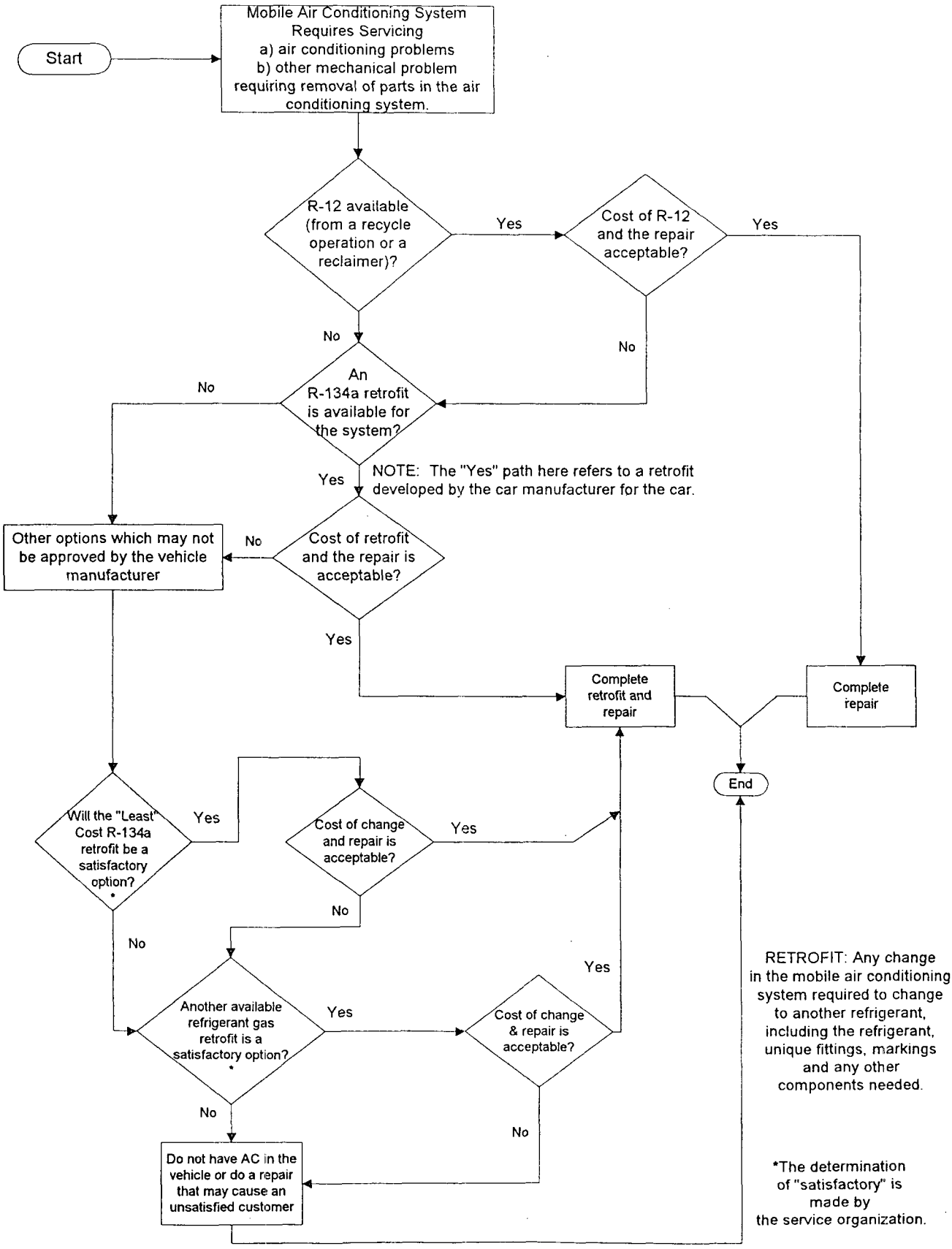
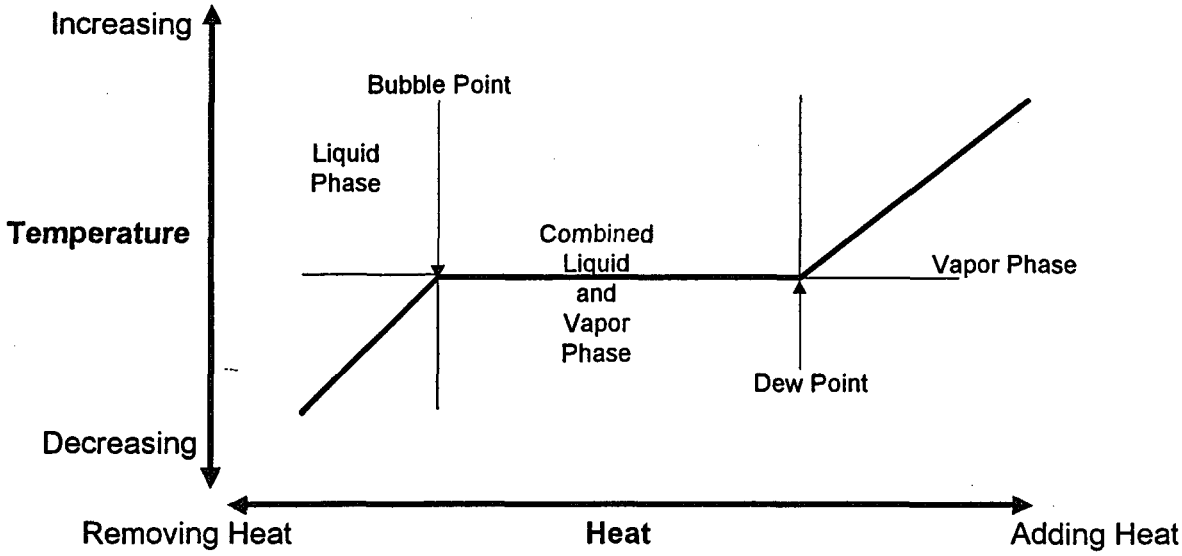
DECISION TREE NO. 1, CAR AC SERVICING

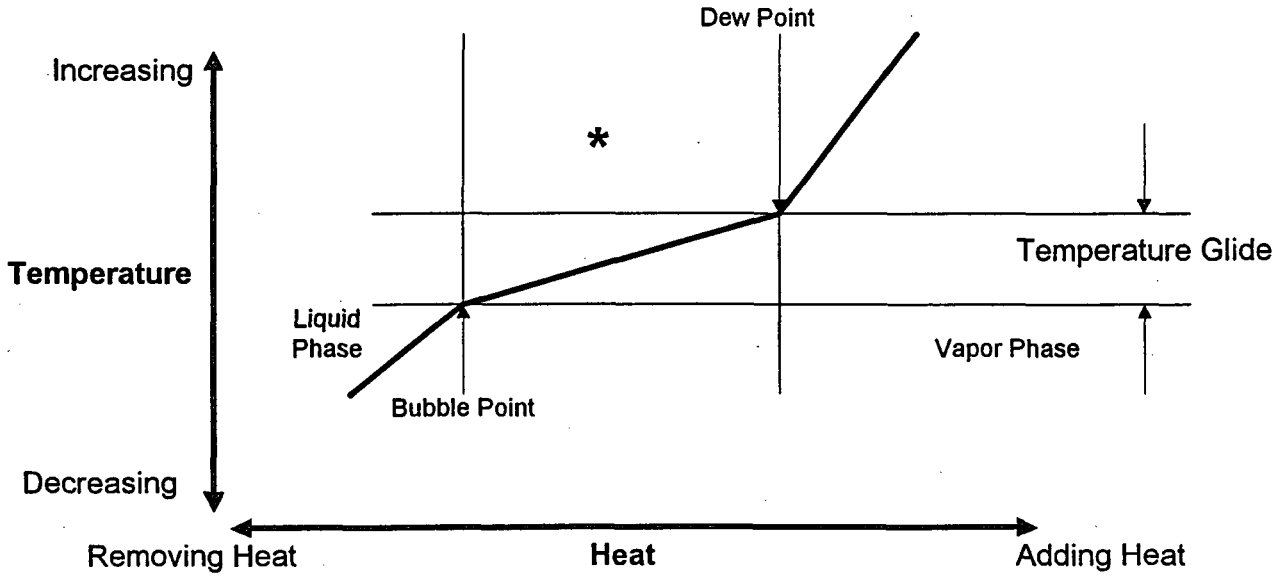


GRAPH 1 SINGLE CHEMICAL



Below the bubble point temperature, only liquid exists. At the bubble point, the liquid begins to evaporate (adding heat). At the dew point, the vapor begins to condense (removing heat) .Above the dew point, only vapor exists. The dew point and the bubble point occur at the same vapor or liquid temperature for a single chemical, but may not for a blend.

GRAPH 2 BLENDED CHEMICAL



* Combined liquid and vapor phase but the composition percentages of the component chemicals will be different than the "as composed" blend composition and the vapor composition and the liquid composition will be different..

NOTE: These graphs assume that the pressure is constant. Similar graphs can be made that assume that the temperautre is held constant (replace the word "temperature" with "pressure" and note a "pressure glide"). Changing both the temperature and the pressure causes a more complex interaction.

CFC Collection Systems for Refrigerant and Insulation Foam and CFC Decomposition System

Yoshiyuki Ishii (Hitachi America, Ltd.)
Tsutomu Hasegawa (Hitachi, Ltd.)
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Shin Tamata (Hitachi, Ltd.)

0. Summary

For the purpose of the Ozone Layer Protection, it is important technology to collect and decompose the existing CFCs contained in the several kinds of equipment. In order to achieve effective collection and decomposition of these CFCs, Hitachi focused on CFCs contained in household refrigerators and has developed and commercialized three systems which are the collecting system for refrigerant CFC, for blowing agent CFC and a decomposition system for collected CFCs.

These systems were installed in a pilot plant for recovering CFCs of the Association for Home Appliances in Japan (AEHA).

1. Introduction

Ozone Layer protection is an urgent global Issue and the Montreal Protocol was agreed upon and amended to phase out Ozone Depleting Substances. For the purpose of actual reduction of the atmospheric chlorine concentration, it is important to collect and decompose these substances since the Montreal Protocol only controls future production of these ODCs and there has been large amount of accumulation of ODCs produced in the past.

Taking account of this background, the most effective way is to collect and decompose ODCs. Therefore, series of systems were developed mainly focusing on the collection and decomposition of CFCs used in household refrigerators.

Old household refrigerators used CFCs as a refrigerant and as a blowing agent for the thermal insulator. Thus, the collection system for the refrigerant CFC, the collection system for blowing agent CFC and the decomposition system for these CFCs are well suited for disposed refrigerators.

2. Collecting System for Refrigerant

The system is composed of three units which are the drilling unit, the separating unit and the recovery unit. Basic system structure is shown in Figure 1.

At an ambient temperature of 20 degrees celsius, approximately 80% of refrigerant is dissolved in lubricating oil. When collection is made of CFC in gaseous phase, it will take more time because the CFC must evaporate from the dissolved oil. Therefore, it is important to collect dissolved CFC in oil. Firstly, a disposed refrigerator is conveyed to the drilling unit. The unit drills a hole in each compressor casing to collect lubricating oil including dissolved CFC.

The separating unit is connected to the drilling unit with high pressure tubing and separates the dissolved CFC from lubricating oil.

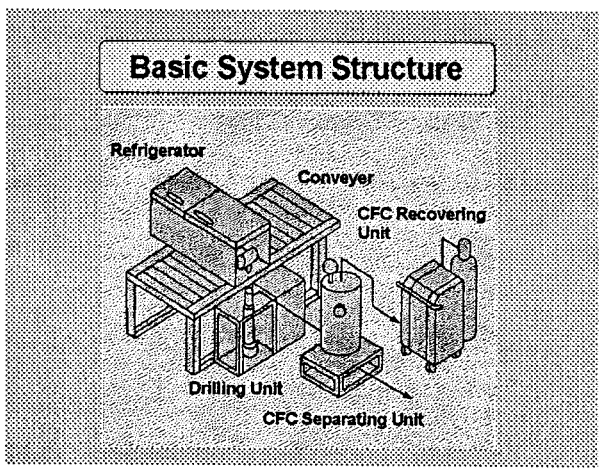

Figure 1

Several features are added in this unit for faster separation of CFC from lubricating oil such as evacuation, heating and agitation.

Lubricating oil is drained and CFC gas is collected by the Recovery unit. If there, the existing Recovery unit may also be used for the collection.

Table 1 shows the specification of the system. The system is compact and easy to transport by small truck and to assemble by connecting three units.

This system enables to achieve higher collection rate and faster collection speed of the refrigerant CFC.

CFC Collecting System Specifications

Capacity:	3 minutes/Refrigerator except the time for mounting
Utility:	Electricity Dried Air 5kg/cm^2
Dimensions:	2,000mm(W) 4,000mm(L) 2,000mm(H)

Table 1

3. Collecting System for Insulation Foam

Two kinds of CFCs are used in household refrigerators, one is CFC-12 and other is CFC-11 as shown in Figure 2. Approximately, 500g of CFC-11 are contained in the thermal insulator. This content is 3 times more than that of refrigerant CFC-12 which is about 150g. This insulator is located between outer steel panel and inner plastics panel as cross section shows. It has very a fine cell structure of polyurethane foam. A magnified picture of the cell structure is shown in the right above of Figure 2. CFC-11 is contained in each cell of the insulating foam. Thus, it is necessary to recover CFC-11 from each cell.

For this recovery, Figure 3 shows the schematic diagram of how CFCs are collected. At the first stage, refrigerant CFC-12 is collected using the system explained above. Next, after removal of the compressor, refrigerator is conveyed to a primary crusher. During primary crushing, cells of polyurethane are broken and CFC-11 is emitted, but the concentration of CFC-11 is not high and a low concentration recovery system collects it.

Next, the refrigerator is crushed at a secondary crusher. At this stage, crushed materials are separated into metal and plastics. After this separation, plastics and light metals are sent to polyurethane tilting air sorter, and separated into polyurethane and other plastics. Separated polyurethane is sent to a fine crusher and each cell of the polyurethane is destroyed. During fine crushing, emitted CFC-11 is collected and crushed polyurethane is compacted to a disk.

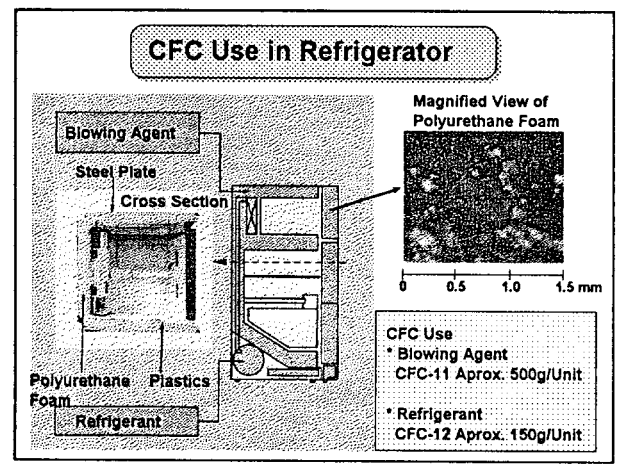

Figure 2

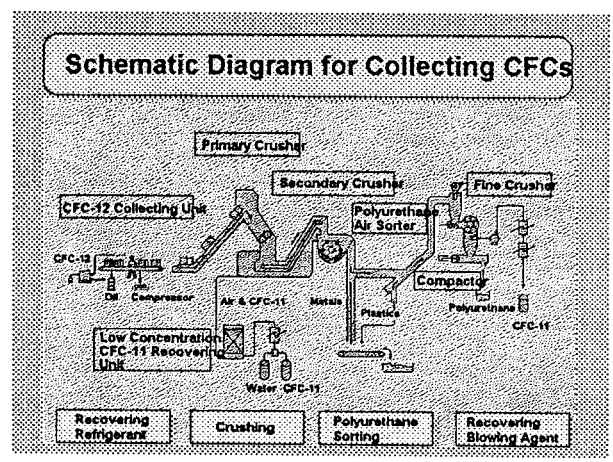

Figure 3

This recovery system is installed at a pilot plant of the Association for Electric Home Appliances Japan (AEHA) in 1996. Figure 4 shows the installed
plant. More particularly, it shows the fine crushing stage of the system.
This system is capable of 3 tons an hour, or approximately, 50 refrigerators can be processed in an hour.

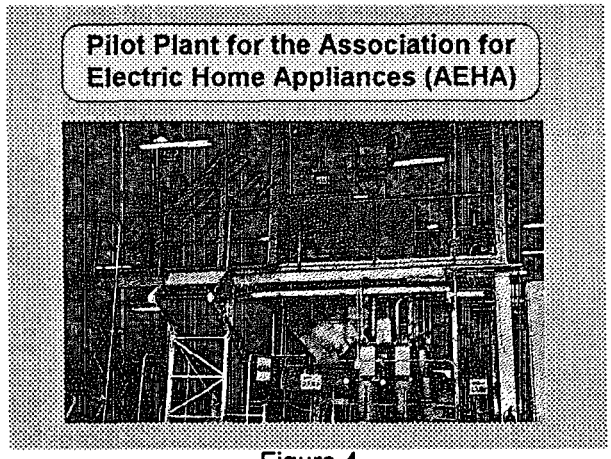

Figure 4

4. CFC Decomposition System

Several approach have been proposed for the decomposition of CFCs such as incineration, plasma decomposition, etc. CFCs are stable chemicals and require a temperature higher than 1,000 degree celsius. Considering energy efficiency for decomposition, Hitachi developed an effective catalyst and transportable decomposition system.

4.1 CFC Decomposition Process

The chemical reaction formula for decomposition of CFC-12 is shown in Table 2. CFC-12 reacts with water and creates hydrogen fluoride, hydrogen chloride and carbon dioxide. In this decomposition process the catalyst plays important role. The first mentioned two chemicals are strong acids and it is necessary to neutralize them.

The second formula shows the neutralization reaction with calcium hydro-oxides. Resulting calcium fluoride and calcium chloride can be used as raw materials

The third formula explains the whole decomposition reaction of CFC-12.

CFC Decomposition Process

Catalyst

$$CCl_2F_2+2H_2O \longrightarrow 2HF+2HCl+CO_2$$

Neutralization

$$2HF+2HCl+2Ca(OH)_2 \longrightarrow CaF_2+CaCl_2+4H_2O$$

$$CCl_2F_2+2H_2O+2Ca(OH)_2 \longrightarrow CaF_2+CaCl_2+2H_2O+CO_2$$

Table 2

4.2 Characteristics of Catalyst

Applying the newly developed catalyst, characteristics with temperature versus CFC-12 decomposition rate are shown in figure 5. This catalyst is capable of decomposing 60% of the CFCs at 600 degree celsius.
99.99% of CFC-12 can be decomposed at 400 degree celsius. Lower temperature decomposition may result in longer life of the catalyst and system as well.

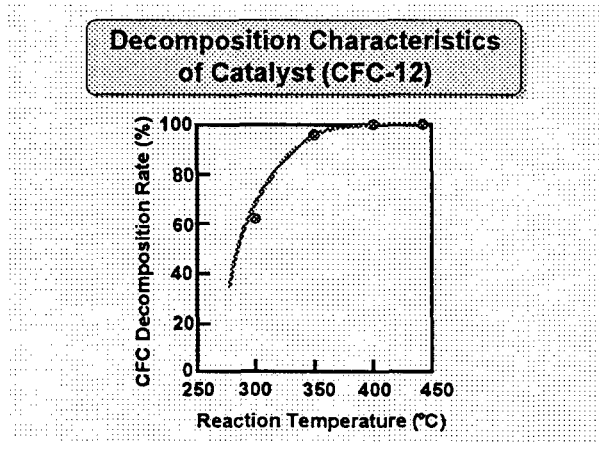

Figure 5

4.3 Schematic Diagram

A schematic diagram of the system is illustrated in figure 6. The system consists of a preheating unit, a reaction chamber, a cooling and absorption vessel, an alkaline chamber, a sedimentation unit, a de-watering unit and a water reservoir.

Preheated air and water are mixed with CFCs and introduced into the reaction chamber containing the newly developed catalyst.

Decomposed chemicals react with the calcium hydro-oxide in the cooling and absorption vessel.

Calcium fluoride and calcium chloride are separated from the calcium hydro-oxide solution at the sedimentation and de-watering unit.

Calcium hydro-oxide stored in the treated water reservoir is returned to the alkaline chamber and reused.

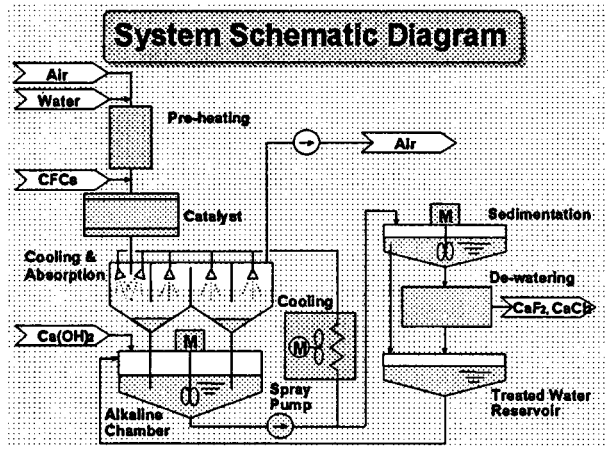

Figure 6

4.4 Catalyst and Sludge

The picture of catalyst is shown in the left side of Figure 7. Decomposed Fluorine and chlorine from CFCs react with calcium hydro-oxide and are finally de-watered. The right picture in Figure 7 illustrates the sludge.
It can be used for raw materials in the chemical industry.

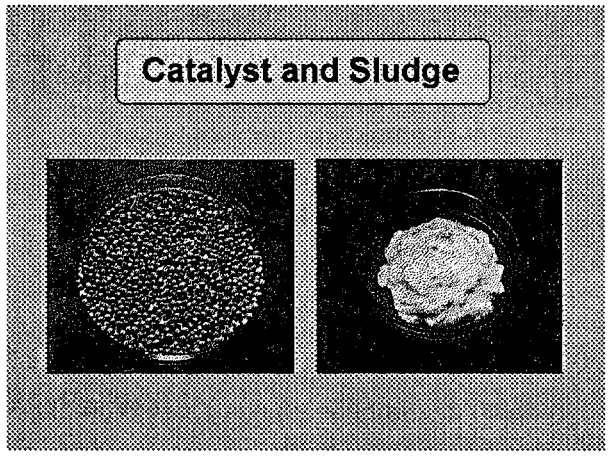

Figure 7

4.5 System Appearance and Specification

The entire system is illustrated in figure 8 and the specifications of the system are shown in Table 3.

The size of the system is so compact that it is transportable by truck.
The consumption of energy is small since CFCs are decomposed at 400 degree celsius.

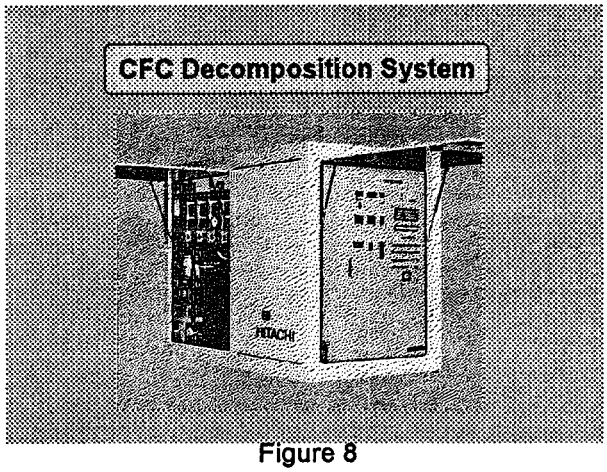

Figure 8

CFC Decomposition System Specifications

Capacity:	1kg/hour(6 hours/day)
Dimensions:	1,600mm(W) 3,000mm(L) 2,200mm(H)
Operation:	Automatic
Utilities:	aprox. 2kw(Electricity) aprox. 30litter/day(Water) aprox. 8kg/day(Slaked Lime)
Others:	Sludge(CaF2 and CaCl2) is recyclable for resources.

HITACHI is ready to supply the unit of which capacity is up to 50kg/hour.

Table 3

Environmentally safe disposal of ozone-depleting CFCs

G. Zehl[1], J. Freiberg, M. Meinke

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1. Introduction

Since their discovery in the thirties chlorofluorocarbons (CFCs) have been widely used, mainly as refrigerants, blowing agents, solvents or cleaning agents because of their outstanding physical and chemical properties such as nontoxicity, nonflammability, their good thermodynamic properties and their low prices. Due to their chemical inertness they are transported to the stratosphere where they are decomposed by UV radiation, and form the reactive catalytic substances that deplete ozon. Chlorine atoms dissociated from CFCs in an altitude of about 18 km are believed to be responsible for diminishing the ozone content of the stratosphere. This would lead to an increase in harmful UV-B radiation reaching the earth's surface.

As a result of these findings the "United Nations Environmental Protection (UNEP) Protocol on Substances that Deplete the Ozone Layer" was adopted in September 1987. An agreement was reached first on a freeze followed by a scaled reduction in the production of CFCs. Owing to the "Montreal Protocol" the production and use of CFCs will be prohibited (as of 1/1/1995 in the European Union and as of 1/1/2030 worldwide).

2. Technological Background

In the middle of the eighties the annual gross production of CFCs was increased to a scale of several million tons. 1986 approximately 10^6 tons of CFCs were produced worldwide. The estimated emissions into the atmosphere were nearly 80 % of this amount. The main application fields of CFCs are shown in Fig. 1. The use of CFCs as refrigerants in equipment with semi-hermetic or open compressors give the main contribution to emission of CFCs. Almost two-thirds of the refrigerant amounts are used for recharging, i.e., to replace refrigerant that has been released.

In order to prevent the further emission of CFCs, the ozone depleting refrigerants still in use have to be recovered, hence methods of collection, disposal and destruction of refrigerants will

[1] to whom correspondence should be addressed

become important. The recovered waste refrigerants have to be replaced by suitable compounds having no ozone depletion potential but affording almost the same thermodynamic properties.

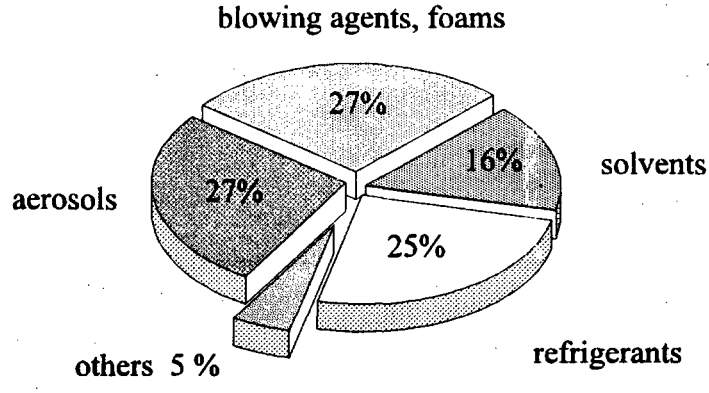


Fig. 1: Applications of CFCs worldwide

In order to speed up the phaseout of the use of CFCs as refrigerants, the midterm transition compounds will be based on HCFCs having only a limited effect on the ozone layer. These so called "Retrofit"blends for the conversion of CFC-12 and CFC-502 plants contain HCFC-22 ($CHClF_2$) as the main substance and can therefore be used with previous equipment and lubricants. However, due to the inclusion of chlorine, they must be viewed as transitional service chemicals only and not as long term solutions for new equipment. The final goal is the use of non ozone-depleting refrigerants based on such compounds as CH_2F_2 (HFC-32), CH_2F-CF_3 (HFC-134a), or CHF_2-CF_3 (HFC-125). Especially HFC-32 or mixtures thereof are thought to be one of the most promising candidates for replacing HCFC-22, which has been mainly used as a low-temperature refrigerant in heavy duty cooling applications. HFC-32 exhibits excellent cooling properties and, in addition, a lower global warming potential than HFC-134a.

Thus the branch of refrigerants faces the task of the environmentally safe disposal of waste refrigerants based on CFCs and the problem of the development and production of currently expensive alternative replacements.

Conventional technologies for the disposal of CFCs are mainly based on non-catalytic decomposition processes like pyrolysis or incineration, and on catalytic decomposition technologies such as catalytic oxidation, hydrolysis and hydrogenation. However, it would be particularly desirable if recovered CFCs were not only decomposed, but converted to harmless and preferably to useful chemicals in a common process. Seeing as there is not enough destruction capacity for the recovered waste CFCs and also that the market for CFC-replacements such as HFC-32 is growing, it is a challenging and profitable task is to convert the waste CFCs into valuable HFCs.

3. Hydrodechlorination of CFCs to HFCs

In contrast to the conventional technologies the selective hydrodechlorination of CFCs provides an alternative CFC disposal to chlorine free hydrogenated fluorocarbons (HFCs). In 1986 the chlorine containing compounds CCl_2F_2 (CFC-12: 42 %), $CHClF_2$ (HCFC-22: 48.5 %) and CF_3-CF_2Cl (CFC-115: 6.2 %) represented almost 96.7 % of the overall consumption of refrigerants in Germany. Now after the coming into force of national regulations these CFC wastes have to be disposed of. They are recovered as pure compounds or as mixtures thereof. By the use of suited catalysts all these waste compounds can be converted into useful HFCs as described in equations 1 - 3:

$$\underset{\text{CFC-12}}{CF_2Cl_2} + 2\,H_2 \xrightarrow{\text{catalyst}} \underset{\text{HFC-32}}{CF_2H_2} + 2\,HCl \qquad \text{(eq. 1)}$$

$$\underset{\text{HCFC-22}}{CHF_2Cl} + H_2 \xrightarrow{\text{catalyst}} \underset{\text{HFC-32}}{CF_2H_2} + HCl \qquad \text{(eq. 2)}$$

$$\underset{\text{CFC-115}}{CF_3CF_2Cl} + H_2 \xrightarrow{\text{catalyst}} \underset{\text{HFC-125}}{CF_3CF_2H} + HCl \qquad \text{(eq. 3)}$$

The resulting HFCs do not have any ozone depletion potential due to the absence of chlorine. Thus, they can be used as alternative refrigerants in industry. The intended process of the selective hydrodechlorination of CFCs should have the following advantages:

- CFCs are disposed of in an environmentally safe way,
- CFCs are used as valuable raw material,
- the produced HFCs can be sold as components of commercial refrigerants (HFC-410 etc.)

The conversion of waste CCl_2F_2 (CFC-12) into the high added value product CH_2F_2 (HFC-32) seems technically and economically feasible with selected metal modified palladium on activated carbon catalysts, which are subjects of several patents. Tables 1 ans 2 show the effect of the substrate on the product distributions.

table 1: Product distribution for the hydrodechlorination of CFC-12 and HCFC-22 at a reaction temperature of 200°C and 250°C respectively

substrate	selectivities [%]			
	alkanes	CH_2F_2 (HFC-32)	CH_3F (HFC-41)	$CHClF_2$ (HCFC-22)
CCl_2F_2 (CFC-12)	19.5	79.1	0.6	0.8
$CHClF_2$ (HCFC-22)	11	87.6	1.4	-

table 2: Product distribution for the hydrodechlorination of CFC-115 at 250°C

substrate	selectivities [%]	
	CF_3-CHF_2 (HFC-125)	CF_3-CH_2F + CF_3-CH_3 + CHF_2-CHF_2 (HFC-134a + HFC-143a + HFC-134)
CF_3-$CClF_2$ (CFC-115)	99.6	< 0.4

The conversion of the substrate was in all cases higher than 98 %. Remaining unreacted CFCs and undesired chlorine containing intermediate compounds were subsequently removed by catalytic purification. When carrying out such a process on a commercial scale one could take profit from the following technological advantages:

- The process is exothermic.
- Depending on the catalysts used one can even dispose of blends of refrigerants as obtained from industry and convert them into high purity products.
- The process works with high selectivity. This makes it attractive even for small enterprises which neither own capacities for CFC-disposal nor for their own production of HFCs.
- The process of hydrodechlorination of CFCs needs only hydrogen and the catalyst, but provides HFCs and industrial acids (HCl/HF) of commercial quality

Such a coupling of waste disposal with the production of alternative refrigerants makes the whole process highly flexible and cost effective, and should therefore be of special interest for enterprises in the refrigeration field which have to dispose of CFCs and own no capacities for HFC-production.

4. Preferred applications of a hydrodechlorination process

4.1. Disposal of CFCs from waste refrigerants

In a pilot plant we will convert the widely used and large scale recovered CFCs freon-12 and freon-502, which is a mixture of 48.8 % HCFC-22 and 51.2 % CFC-115. Due the difference between the reactivities of CFC-12 and CFC-115/HCFC-22, freon-12 and freon-502 have to be treated under different reaction conditions (cycles A,B). The concersion of CFC-12 gives 99 % HFC-32. HFC-32 itsself represents a commercial product (freon-32) that is used as low-temperature refrigerant in heavy duty cooling applications. The conversion of freon-502 gives a mixture consisting of HFC-125 and HFC-32. In this case marketable freons-410A,B can be obtained by adding controlled amounts of HFC-32 from cycle (A) to the products of cycle (B). Our concept of process design further involves the possibility to introduce commercial available freon-134a. This expands the variety of products by the freons-407A,C.

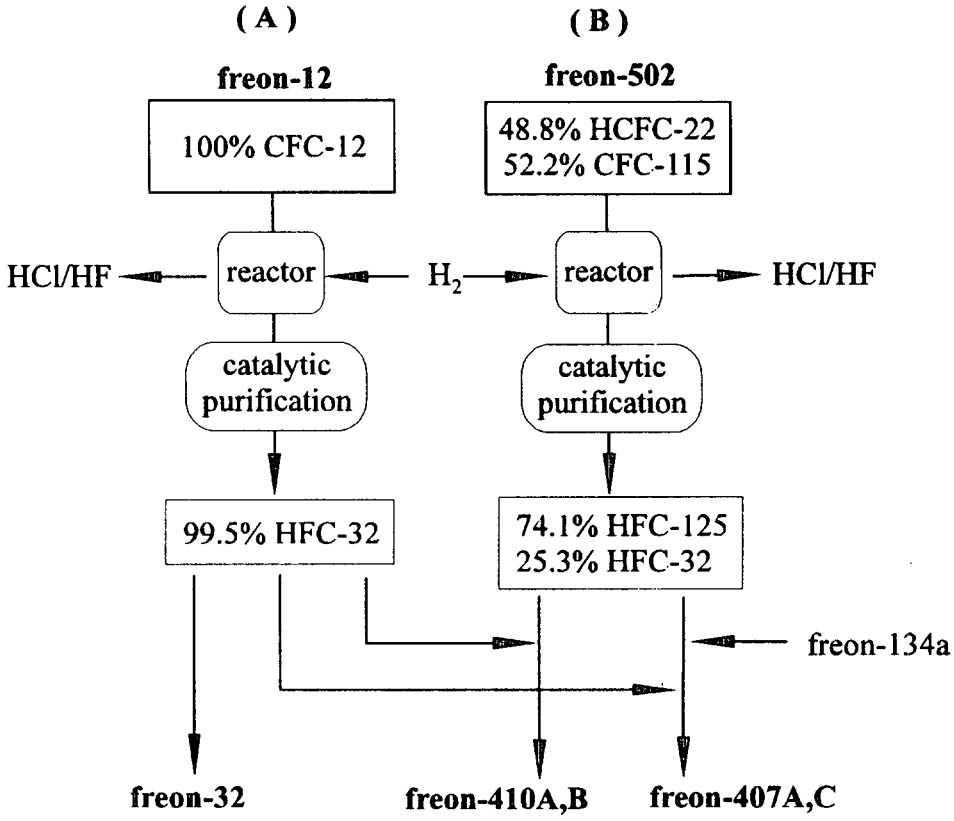
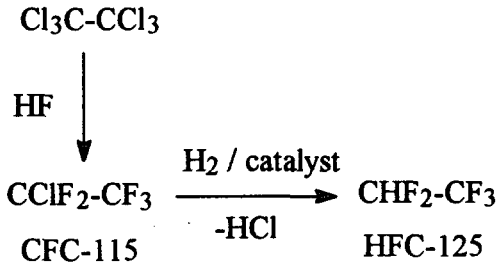


Fig. 2: conversion of waste refrigerants into chlorinr free replacements

4.2 Conversion of CFC-115 production lines to manufacture of HFC-125

CFC-115 (ClF_2-CF_3) is manufactured on an industrial scale by the fluorination of hexafluoroethane with hydrogenflouride (HF). These plants could easily be transformed to produce HFC-125 (CHF_2-CF_3) by attaching an additional hydrodechlorination step, i.e. converting the primary product CFC-115 into HFC-125. Thus, the existing production plants for CFC-115 could be used for the manufacture of ozone safe refrigerants.



This would decrease the investments necessary for the setup of new production lines which are important for the speed up of the phaseout of production and use of CFCs, especially in the countries of eastern Europe and Asia. According to international agreements, today's annual production of about several thousand tons of CFC-115 in that countries should be reduced to zero by the year 2030.

4.3. Purification of conventionally produced HFCs

Generally HFCs are produced from the respective chlorinated hydrocarbons by fluorination treatments using selected catalysts in the liquid or vapour phase. Due to that method of production the product gas stream always contains traces of chlorine containing intermediate products. A catalytically purification treatment could simplify or even avoid the expensive distillative separation of this contamination.

The above mentioned undesired chlorine containing contamination can be reduced to several ppm without significant loss of the valuable HFC. Such purity is important for special applications like propellants for medical sprays. Today CFC-12 is still used for these applications. Its substitution for HFC-32 is a challenging task. Medical applications will create a growing market in the next years.

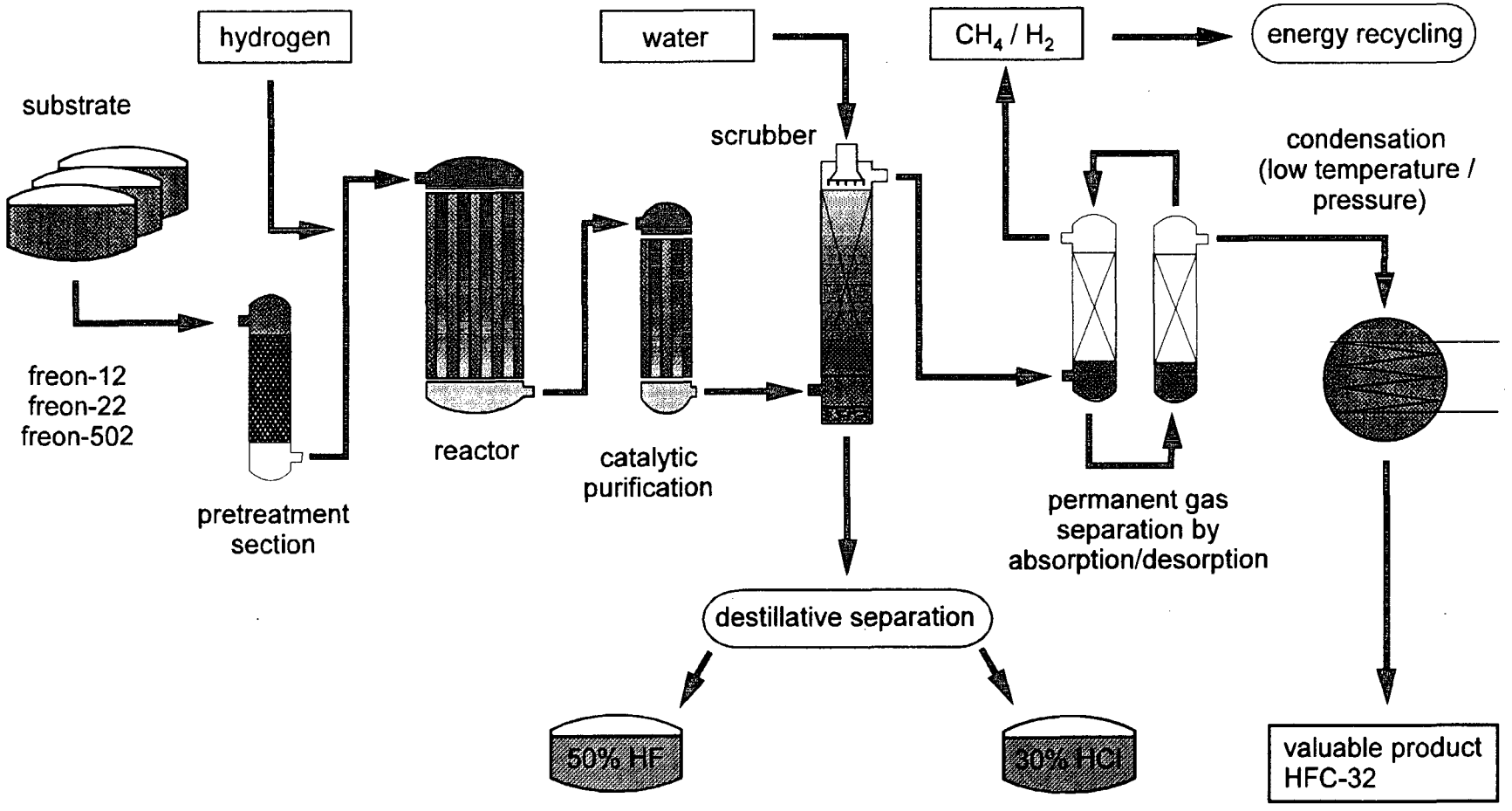


Fig. 3: Block sheme for the process design for the hydrodechlorination of CFC-12 (CCl_2F_2)

5. Process design

A process design for the selective hydrodechlorination of CFCs has been made based on a capacity of 1 kg/h. Important design considerations are the exothermicity of the reaction and the need for the removal of HCl/HF and H_2/CH_4 from the products. The technical feasibility of the complete process design was proved on a laboratory scale. No unsurmountable barriers were encountered. A scheme of the designed process is depicted in Fig. 3.

The feed of the plant consists of recovered waste CFC-12, waste HCFC-22 or CFC-115. These raw materials contain contaminants such as oil or water which must be removed by a pretreatment before the feed enters the reactor. Because of the highly exothermic reaction a multi-tube liquid cooled fixed bed reactor has been chosen. The heat transfer fluid allows reaction temperatures in the range of from 150°C up to 300°C, depending on the substrate being fed.

Because of the large difference in the reactivity between CFC-12 and HCFC-22, a recycling of the intermediate product HCFC-22 is not useful and a one time operation with 100% CFC conversion is preferred. In order to reach complete conversions, an additional catalytic purification step is used. Using a special hydrodehalogenation catalyst, the intermediate products HCFC-22 and HFC-41 (CH_3F) are converted to methane. The loss of the target compound HFC-32 during this purification step is less then 1 %. Thus the product gas stream contains only HCl/HF, alkanes and excess hydrogen in addition to the target product.

Therefore the further product purification is divided into two steps. First the acids (HCl and HF) are removed from the gas stream and subsequently the permanent gases methane and hydrogen are separated from the target HFCs. The HCl and HF are scrubbed with water to yield a mixture of aqueous hydrochloric and hydrofluoric acid. A destilative separation yield the pure acids. This is state of the art. The permanent gases are separated by an absorption/desorption step. The desorbed fluorocarbons are pressurized and condensed. The liquefied component is then pumped away and filled to gas cylinders.

6. Conclusions

Waste refrigerants recovered from industry, such as freon-12, freon-115, freon-502 and freon-22, can be easily converted into the valuable chlorine free products, which may be recycled into the market.

A high selectivity to HFC-32 can be combined with a complete CFC-12 conversion by using an additional catalytic purification step. Thus the conventional extensive purification by pressure distillation or low-temperature distillation can be avoided. The content of the toxic HCFC-31 in

the target HFC-32 is below 10 ppm, which also makes the HFC-32 attractive for medical applications.

A pilot plant with a capacity of about 1 kg/h was designed and will be tested for the conversion of waste freon-12 into HFC-32 within this year.

The preliminary process design has shown that the conversion of CFC-12 into the high added value product HFC-32 is both technically and economically feasible. The design can easily be extended to a process for conversion of both HCFC-22 and CFC-115 into HFC-32 and HFC-125 respectively.

A process based on the investigated catalyst systems could be an important tool in the protection of the ozone layer. The selective hydrodechlorination using heterogeneous catalysts thus represents a technologically promising and economically valuable contribution to solving the global problem of ozone depletion.

Acknowledgements

I would like to express my gratitude to the Ministry of Economy of the Federal Republic of Germany and the Ministry of Environmental Affairs of the Land Brandenburg for their financial support.

Tests of Supermarket Display Cases when Operating with Secondary Refrigerants

Wilson Terrell Jr., Yanhui Mao and Pega Hrnjak*

Abstract:

The objective of this paper is to present a comparison of display case performance when operating with single phase secondary fluids to baseline mode at low temperatures (-15°C to -30°C). Baseline mode is the operation when refrigerant R404A evaporates in a DX evaporator located in the display case.

Tests are carried out at the Commercial Refrigeration Laboratory, University of Illinois Air Conditioning and Refrigeration Center. Tests are conducted according to the procedure described in ANSI/ASHRAE Standard 72 - 1983 "Method of testing open refrigerators for food stores" (hereinafter abbreviated as Standard).

Tests shown here are conducted on a 8 ft long single deck low temperature display case. The display case is defrosted by a electrical resistance heater in baseline operation and with warm secondary refrigerant in indirect refrigeration mode. The same heat exchanger is used for both test.

Introduction:

The approximately 30,000 supermarkets in the United States account for about 20% of CFC refrigerant consumption in this country [Duffy 1990]. Typical leak rate reduced from early 40% just few year ago to 15% [Harrison 1995, Gage 1997] is stil significant and put this indrusry second to automobile A/C systems in refrigerant leakage. Implementation of secondary refrigeration loops is sound way to reduce refrigerant leaks and to open prospective for differenet primary refrigerants. Issues of allegedly lower efficiencies of indirectly refrigerated systems and display cases are still open. In order to contribute understanding this issue EPA, Hussman and Tyler sponsored the project at Air Conditioning and Refrigeration Center, University of Illinois.

Test facility and procedure

Environmental Chamber:

Two display cases are placed in the environmental chamber built to meet Standard requirements for testing display cases. The chamber is made out of polyurethane sandwich panels with a thickness of 3 3/4 inches. According to the Standard the environmental chamber has white gloss walls, air velocity is 0.14 m/s at 3 m from the floor (req. max. 0.25 m/s) and is iluminated by fluorescent bulbs 836 lux (required min. 800 lux).

The schematic of the environmental chamber is given in the figure 1. Air flows from the ceiling through twentyfour distributors. Return air enters six vents at the bottom of the chamber.

* W. Terrell Jr. is Graduate Research Assistant, Yanhui Mao Research Engineer and Pega Hrnjak Assoc. Director ACRC and Adj. Asst. Professor, all with Air Conditioning and Refrigeration Center, The University of Illinois at Urbana - Champaign.

The refrigerated case is operated in the prescribed ambient environment (T_{db} = 23.9 ± 1.7 °C, T_{wb} = 17.8 ± 1.7 °C). Conditioning of the circulating air (heating and humidification) is completed before entering the blower.

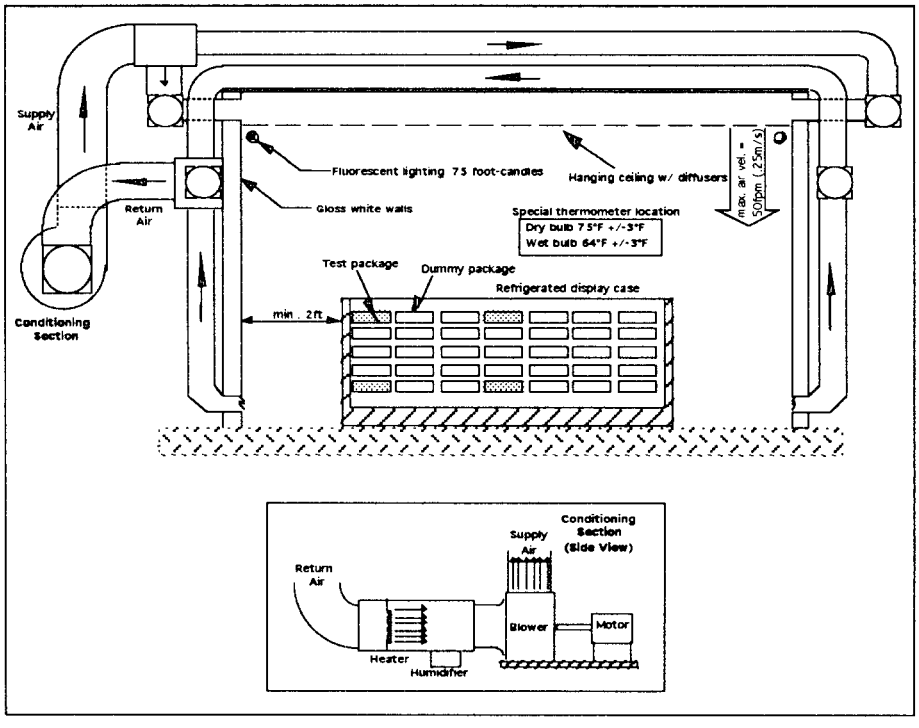


Fig. 1. Experimental Test Facility - Environmental Chamber

More information about the test procedure, calibration and test results could be found in the report [Hrnjak,1997].

Procedure for Baseline Test:

Adequate refrigerant flow to have minimum superheat for stable operation and liquid refrigerant temperature is supplied as demanded by the case. This is achieved by changing the suction pressure and adjusting the thermo expansion valve to obtain maximum flow rate and still keep superheat stable. The display space is filled with test packages and dummy packages. After repeatable conditions occur, the recorded data for a 24 hour period is treated as one test level (defined by Standard). Repeatability of test conditions are determined by ± 0.2 °C difference in package temperatures at the beginning and end of the 24 hour period. Package temperatures generally take longer to reach steady state compared to other parameters (air and refrigerant temperatures).

The schematic of the test facility in baseline mode is shown in figure 2. Two compressors are in parallel for which only one operates at a given time. The condenser is shell and tube water cooled.

Procedure for Tests with Secondary Refrigerant:

For test with secondary fluids, two additional evaporators (one brazed plate and other shell and tube) were added in parallel to the condensing unit to serve as the chiller for the fluids.

The secondary loop shown in figure 3 consist of two sections, the "cold" loop (refrigerating loop) and the "warm" loop (defrost loop).

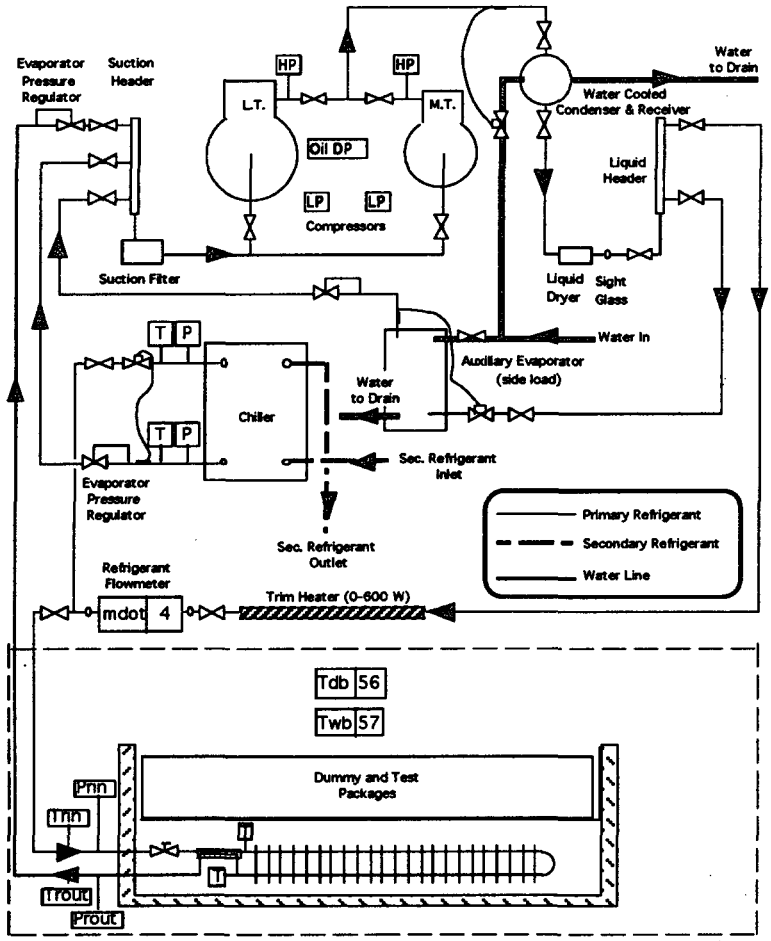
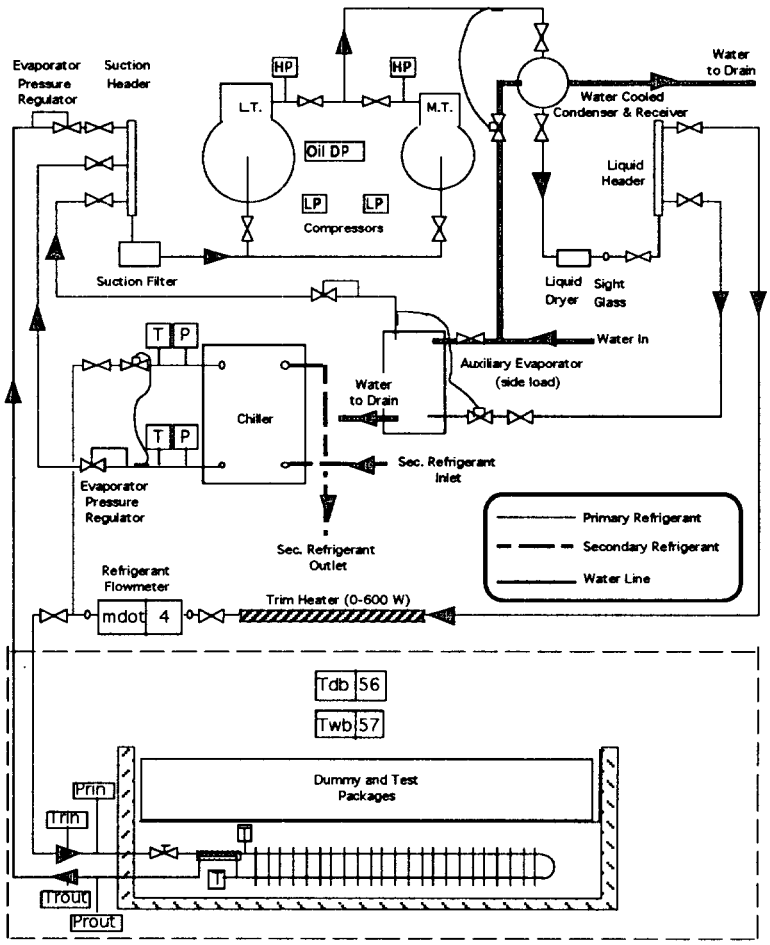


Fig.2. Baseline Schematic

The "cold" loop serves to provide refrigeration in the test period. Secondary fluids are cooled in the chiller (brazed plate or shell & tube evaporator). The fluid is pumped from an expansion tank through coaxial heaters. Last heater is used for fine adjustment of the fluid temperature and also for on-line determination of the specific heat of the secondary refrigerant. The fluid then enters the display case and flows back into the heat exchanger. Temperatures are measured with thermocouples at the inlet, coil passes, and outlet. The pressure difference across the heat exchanger is measured using a pressure differential transducer. The mass flow rate is measured using a Co riolis type mass flow meter at the exit from the display case.

The "warm" loop consist of two coaxial heaters, an immersion heater, an expansion tank, and the pump. Some time before defrost of the display case, the heaters are turned on to warm up the fluid. This fluid is circulated around the loop at the starting temperature until defrost starts. When defrost begins, valves are switched so that hot fluid enters the display case (while the cold loop is closed). When defrost is completed, the system is switched back to the cold loop. All conditions that applied to the baseline test (based on the Standards) apply to secondary test.

Test with secondary refrigerant has coolant velocity as the additional parameter compared to baseline tests. At low temperatures most fluid candidates considered can not be operated in turbulent mode with a reasonable pressure drop.



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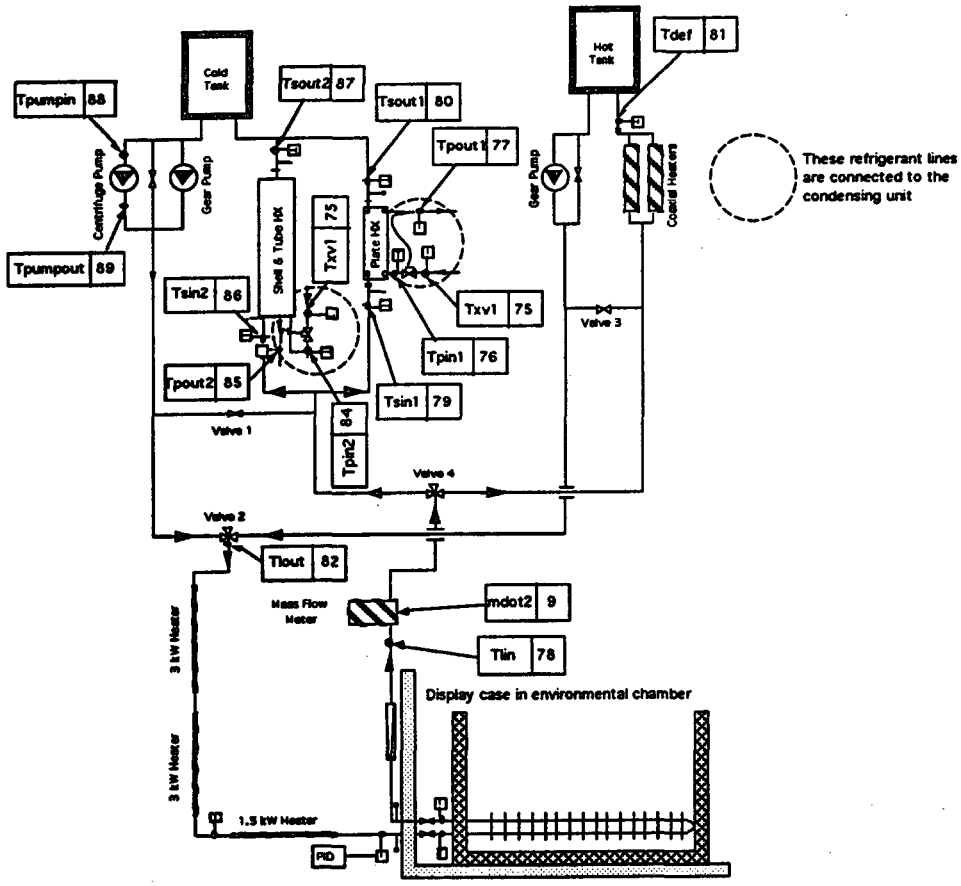

Fig. 3. Schematic of the Secondary Loop

Fluids Tested:

Several fluids were tested: R404A (as a baseline fluid), HFE (should be tested further - data are not included in this paper), potassium formate, and potassium acetate. Additional tests are in progress. Results shown here are mostly for potassium formate. Why these fluids?

The ideal secondary refrigerant should be: nontoxic, nonflammable, environmentally friendly, safe for contact with food, stable, compatible with common engineering materials, and have good thermophysical properties (high specific heat, high thermal conductivity, low viscosity, 5 to 10 cP, and high density) at low operating temperatures (-40°C).

Application range below -20°C and as low as -40°C is characterized by the existence of just a few real candidates, none of them being perfect. Silicon oils (polydimethylsiloxane), hydrofluoroether, some brines (potassium acetate, potassium formate). The trade-off for single phase candidates is in specific heat and viscosity: fluids with high specific heat have high viscosity and vice versa. Here is the brief overview.

Silicone oils

Applied in pharmaceutical industry, some industrial and commercial installations silicone oil has unfavorable thermophysical properties at low end (-40°C) compared to organic salts and hydrofluoroethers but are better than glycols. They are combustible. There is significant experience in different applications.

Organic salts (Potassium Formate and Potassium Acetate)

These are new brines and there is no significant experience in real applications. There are some problems with material compatibility but they have very good thermophysical properties, especially when compared to other candidates at low end of temperature range (-30 to -40°C).

Hydrofluoroethers

These have low viscosity at low temperatures and it is important that viscosity does not change significantly at low temperatures. These the only candidate of those mentioned here that could be used even at -100°C as a technically reasonable secondary fluid. They have poor specific heat, good material compatibility but some GWP.

Initial testing began with the most promising candidates. Silicon oils are excluded due to flammability as some other fluid not described here (d-limonene, ethanol, etc.)

Secondary refrigerants were tested in concentration needed for -40°C: potassium formate with 45% and potassium acetate with 50%.

How to compare performance of the display case when operating with different refrigerants?

Approach taken in this project is to use existing, state of the art display cases, run the baseline tests with refrigerant and oil as in conventional operation, and compare it later to operation with single phase secondary refrigerant. Two steps in testing display case with secondary refrigerant are taken:

1. With heat exchanger same as evaporator substituting distributor with the inlet header and
2. With a modified heat exchanger which is more suited to single phase secondary refrigerant (fin and tube spacing, circuiting, etc.).

Data shown here are the part of the first step. Heat exchanger surface when operating with secondary refrigerant is reduced by removing suction line heat exchanger used in baseline tests.

One of the key issues is what criteria will be used to compare the fluids. Our approach is to compare performance based on product temperature because the purpose of the display case is to maintain product temperature at required level. Some objection could be raised due to the fact that it is easier to measure air temperature in real applications (in a store).

Standard prescribes presentation of three package temperatures: the coldest test package average (average temperature of the coldest package in the test period), the warmest test package average and integrated average. The coldest test package is usually at the bottom of the display case (P4), right above the evaporator (heat exchanger), while the warmest package is on the top (P8 or P2). The critical temperature is obviously the warmest test average. Figure 4 shows the position of test packages in the display case.

The performance of the heat exchanger is monitored in order to collect data useful for the heat exchanger optimization. Figure 5 shows the positions of the thermocouples attached to the heat exchanger.

Some Test Results

Operating temperatures:

Figure 6 shows the performance of the display case when operating with R404A and with potassium formate as the secondary refrigerant.

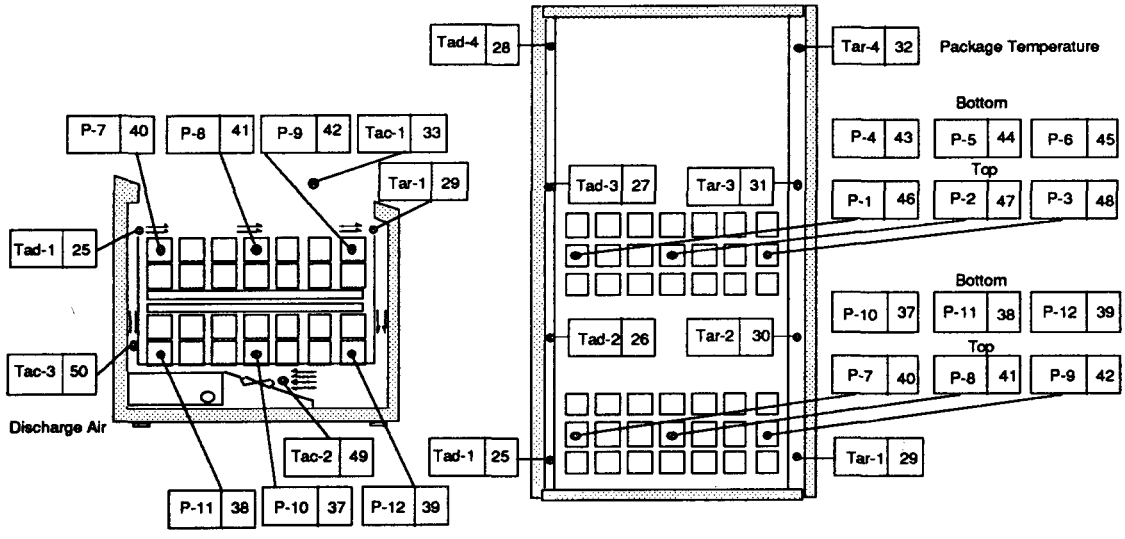

Fig. 4. Position of the test packages in the display case

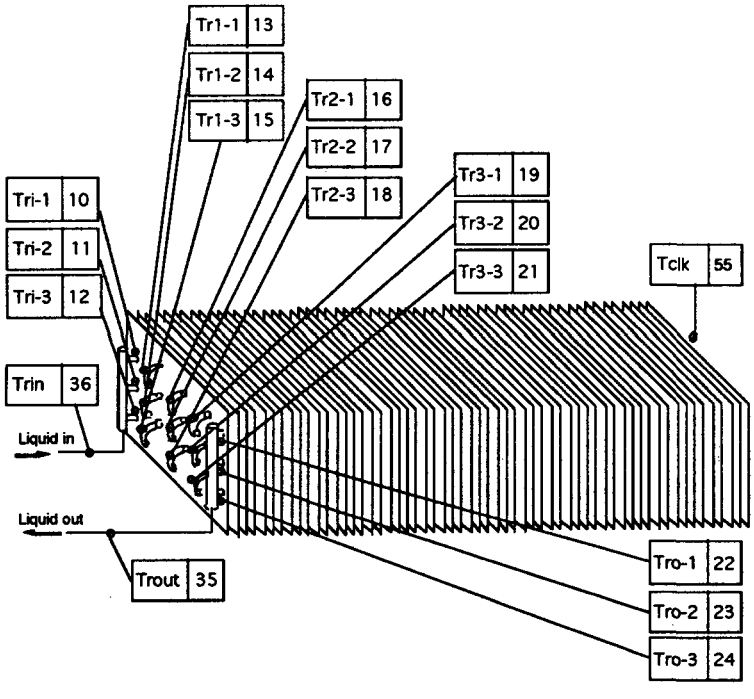

Figure 5. Heat exchanger thermometer positions

Temperature at the inlet to the evaporator for both baseline and indirect refrigeration mode is displayed at the abscissa while ordinate represents the package temperatures. Three lines are shown for each refrigerant. Dashed lines represent performance in baseline mode, while solid lines represent performance with the secondary refrigerant (potassium formate). This diagram shows that the same product temperature could be achieved by significantly higher temperature of the secondary refrigerant at the inlet to the coil.

For example, to maintain required frozen food product temperature in conventional store evaporation temperature of R404A is typically -28°C. At this case in our baseline tests discharge air temperature is -24°C °C and the temperature of the warmest test package is -7°C. The same product temperature could be achieved with potassium formate at the inlet of only -20.5°C. In ice-cream low temperature range difference is reduced. At -10°C warmest test package temperature the

increase of operating temperature at the inlet is from -32°C in baseline to -27.5°C. At lower end this difference gets even smaller

Tests with secondary refrigerants are conducted with different fluid velocities in the heat exchanger. Neither potassium formate nor potassium acetate could run in turbulent mode with reasonable pressure drop. Since heat transfer coefficient in laminar regime is not a function of the velocity, only the glide has influence to the heat transfer. There is the question of what flow rate would give the optimum between heat transfer and pressure drop. Figure 6 indicate that lower velocities are closer to the optimum. Graphs show package temperatures for two flow rates for each secondary refrigerant.

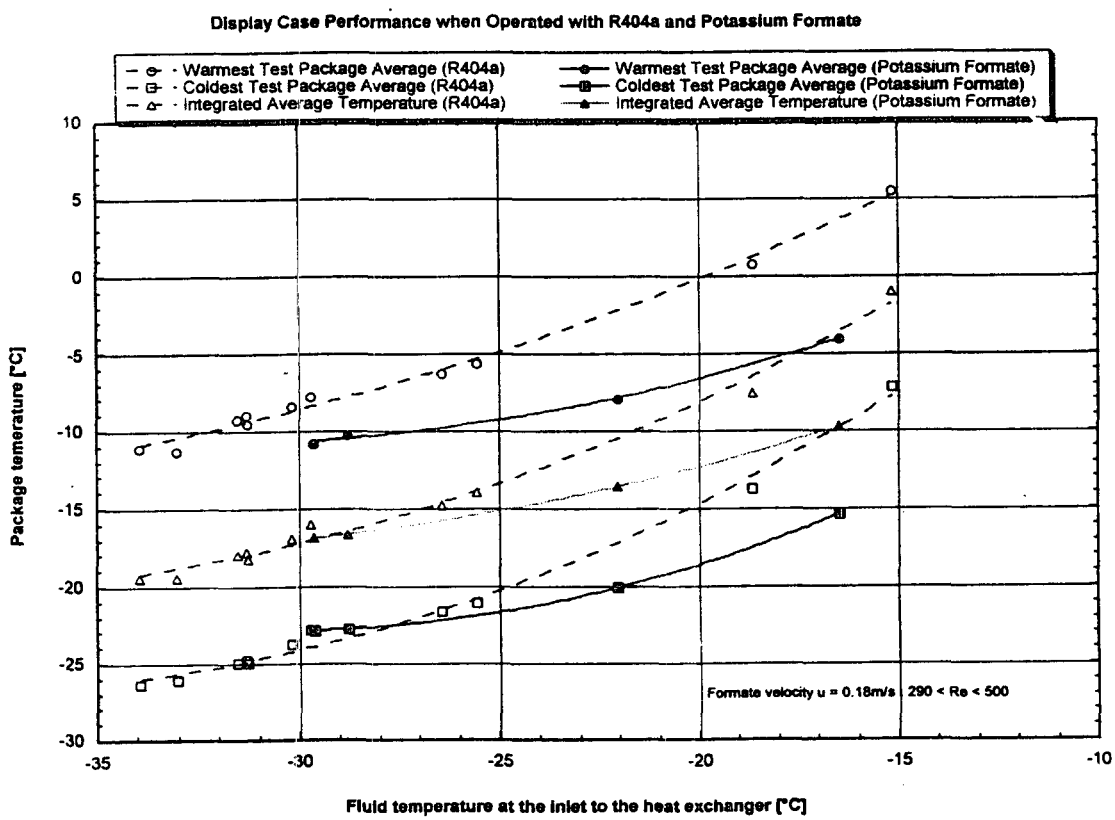

Fig. 6. Package temperatures as a function of the inlet temperature to the heat exchanger

Defrost:

Experiments show that the defrost period is significantly reduced when warm secondary refrigerant is used instead electrical heaters to melt the frost.

For baseline tests, the range of defrost time was from 12 to 21 min. The termination of the defrost cycle was controlled by a clixon installed on evaporator pipe.

Defrosting of heat exchanger served with secondary refrigerant goes through phases:

1. Pipes are defrosted first in app. one minute. It is the time for secondary refrigerant to flow through the coil.
2. Fins are defrosted in next 2-3 min.

3. Drip pan requires more time to defrost. Termination signal was set at 10°C for the critical position between the fan cover and the drip pan.

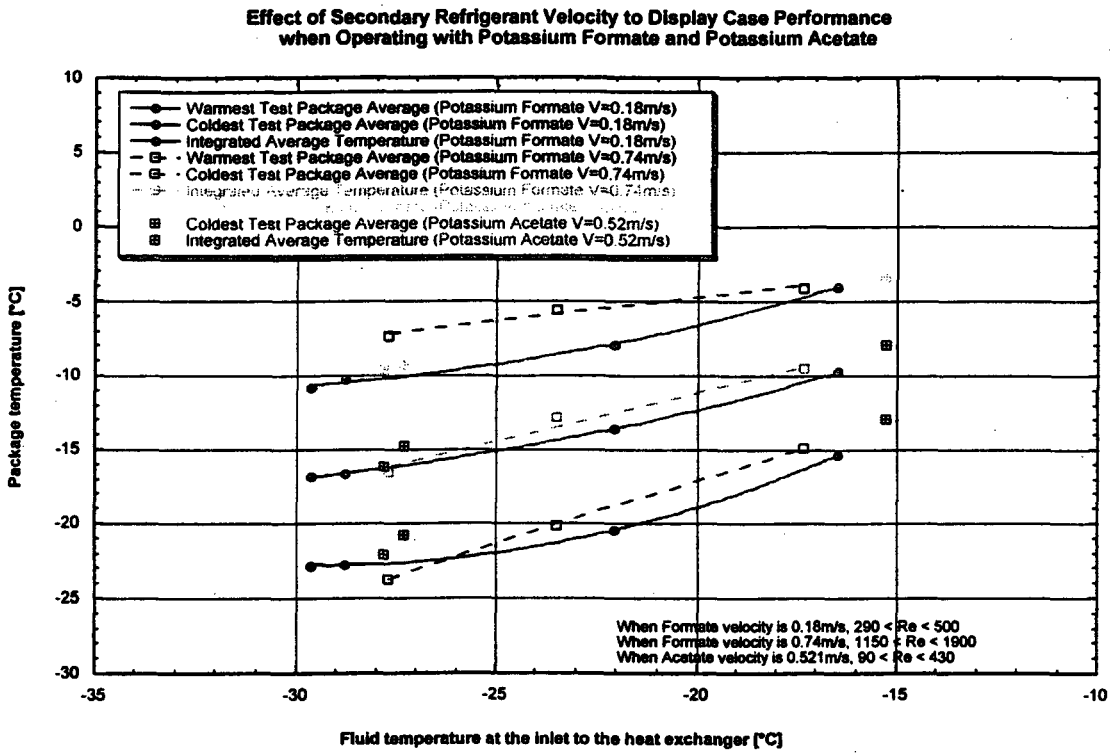

Figure 7. Effect of velocity on package temperature when case is served with potassium formate and potassium acetate

Total defrost time is 10 to 15 min. due to slow drip pan defrost. This could be improved by adding additional small defrost heater similar in design to those used in cool gas defrosted cases. There is no reason why total defrost time could not be just slightly longer than time needed for fin defrost.

Inlet temperature of the secondary refrigerant was 30°C and the flow rate was slightly higher than in the refrigeration mode.

Reduction of defrost time has several positive effects. One is more uniform temperature profile in the product stored in display case.

Figures 8 and 9 show the typical temperature profiles for air and packages in the same display case when operating at similar product temperatures in DX (conventional) mode and in secondary loop mode.

Figure 8 shows the difference in temperatures of the packages at the different locations in the baseline (DX) mode both before and during the defrost. The temperature in the center of the coldest package is being changed by approx. 8°C during the defrost. This change is greater at lower operating temperatures for colder packages. At higher operating temperatures warmer packages (more exposed to the ambient air) experience greater change in temperature during the defrost.

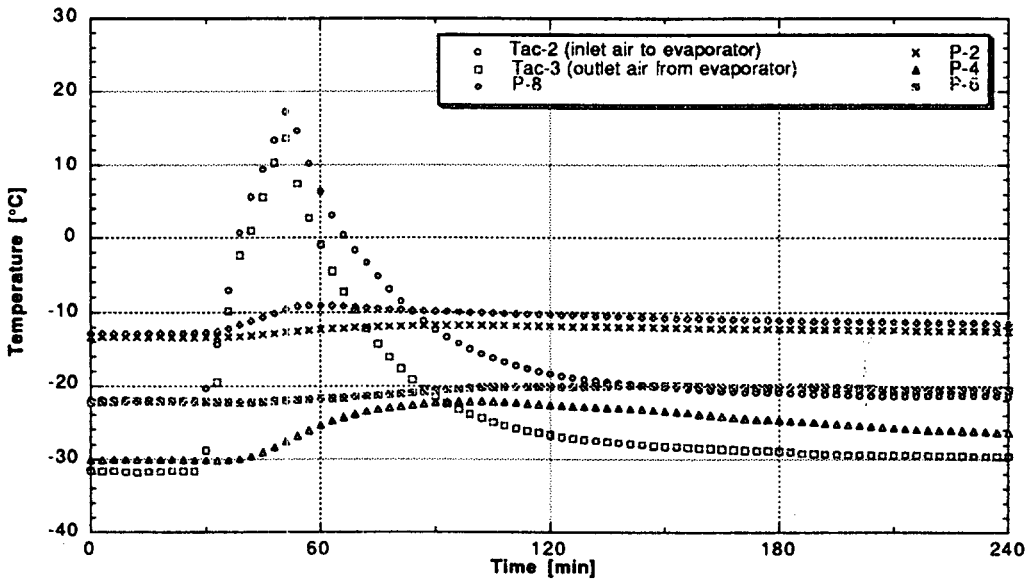

Figure 8. Temperatures of the coldest packages in the display case (P4, P6) and the warmest (P2, P8) and air in and out from the evaporator (Tac-2 and Tac-3) in defrost period. Defrost by electrical heater. Refrigerant is R404A. Greatest variation in P4 temperature is approx. 8°C

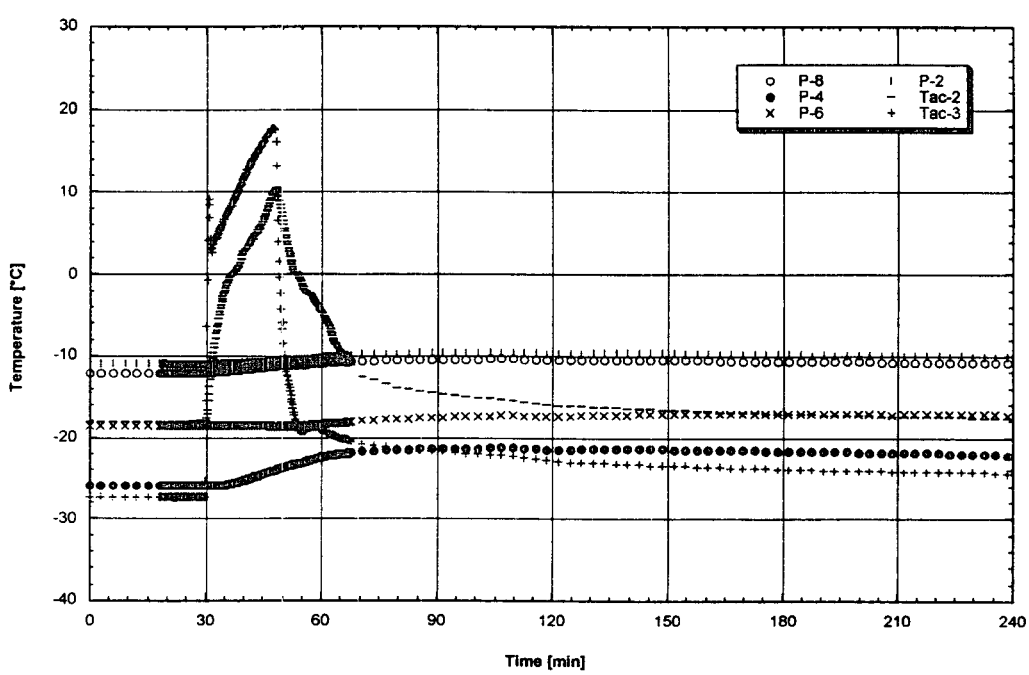

Figure 9. Temperatures in the same display case as shown in Figure 10 but refrigerated by cold brine. Defrost is by warm secondary refrigerant. Greatest variation in coldest package temperature (P4) is lower - approx. 4.5°C.

Comments on performance

Figure 6 shows that the same product temperature could be achieved with a higher temperature of the secondary refrigerant compared to evaporation temperature in baseline mode. Also the load is reduced due to more efficient defrost. Shorter defrost time decreases heat input into the refrigerated space (heat load later) and increases effective running time (refrigeration capacity).

Higher coil surface temperatures are beneficial and should cause less frost. The temperature glide (due to finite specific heat) and almost constant heat transfer coefficient on the refrigerant side results in more uniform frost deposition. More uniform frost will allow for greater fin density (more surface in the same volume). Additionally, more uniform frost results in a smaller reduction of air flow as defrost time is being approached, thus increasing both air side heat transfer and temperature difference compared to operation in DX mode.

The defrost cycle should be terminated when the last ice particle is melted from the fins. Therefore, uniform frost deposition exhibits another advantage in shortening the defrost period. For less uniform cases part of the evaporator is overheated in order to allow defrost of the part having thicker frost initially.

It should be noted that results shown here are for the display cases served with secondary refrigerant only, not for the whole system. Nevertheless some authors [Arshansky, 1997] reported a slightly better system COP in supermarket with secondary loops compared to predicted performance of refrigeration system operation in conventional mode. Other authors [Nyvad, Lund, 1996] claim reduction in consumption of electrical energy for a store when an old R12/R502 system was retrofitted with ammonia chillers having secondary loops at both high and low temperature. This new ammonia system is slightly more efficient then conventional counterpart and does not have electrical but warm liquid defrost. Superheated vapor from compressor discharge is used to heat liquid for defrost. Some other supermarket secondary loop systems report increase in energy use from 5 to 20%. The general expectation is that this penalty will be reduced as systems with indirect refrigeration become simpler and cheaper to build in the future.

Conclusion:

Test results shown in figure 6 show that the performance of the display case served with potassium formate at low temperatures is better than in baseline mode (using the same evaporator as a heat exchanger). Results are encouraging and tests are continuing with new fluids and better designed heat exchangers for the single phase secondary refrigerants.

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Development of Scroll compressor of Commercial and Industrial Air Conditioner Used for R407C refrigerant

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【ABSTRACT】

Recently, there is an urgent demand for air conditioning and refrigeration compressors that use the new refrigerant R407C instead of R22. Thus, the comprehensive evaluation of candidate refrigerant oils; stability, miscibility and lubricity, were carried out in order to use R407C. As a result, polyvinyl ether (PVE) was selected as the most suitable oil for R407C.

In order to use R407C , it is necessary to modify the conventional scroll compressor (that use R22) So, this paper describes the newly developed compressor and the details of modification for the use of R407C and PVE.

Here are the following problems for the compressor itself

i) Decline in reliability of sliding parts : since R407C does not contain chlorine.
ii) COP reduction : the COP of R407C is 7% less than that of R22 in our initial tests .
iii) Increase in oil circulation : this is a new problem of PVE, the mixture of R407C and PVE has revealed weak oil separation.

As for the decline in reliability, PVE was selected as the most suitable lubricant ,then the further improvements were carried out ; application of lead-bronze metal to the bearing to prevent seizing and severe wear, changing the oldham coupling material to a Si-rich aluminum alloy for severe anti-wear.

Next, for COP reduction, the design compression ratio of the scroll was increased in order to adapt the pressure increase associated with using R407C instead of R22 ,and the shape of the scroll center was changed to reduce the over-compression loss.

Finally, for the oil circulation, dimpling the demister in the higher pressure chamber increased the efficiency of oil separation.

These developments prevent the peculiar lubrication troubles caused by HFC refrigerants, succeeded in a 3% increase of COP, and reduced the oil circulation rate by about 70%.

【INTRODUCTION】

There are some problems associated with the change from HCFC refrigerants to HFC refrigerants. One is a decline in the reliability of sliding parts used for HFC's. As for this serious problem, some reports have already suggested that the peculiar lubrication

troubles with sliding parts when used with HFC's occur more often than for HCFC's since HFC's do not contain chlorine.[1] Second, the COP of R407C was 7% less than that of R22 in our initial tests because of the reduction of theoretical COP (5.4% less compared with R22), because of the difference of the viscosity of these oils and the difference of operation pressure of these refrigerants. Third, this is a new problem with PVE that was found during development, the oil circulation ratio of R407C is over two times larger than that of R22.

The purpose of the development is to solve the above mentioned problems in order to use R407C.

【THE DEVELOPED COMPRESSOR】

A section of the newly developed scroll compressor and the modifications are shown in Fig.1. The motor is placed in the lower pressure chamber. The refrigerating capacities for the newly developed series of compressors and the new inverter compressors range from 26,200 to79,600 BTU/H (at ARI,60Hz).

【SOLUTIONS FOR PROBLEMS ASSOCIATED WITH R407C AND PVE】

RELIABILITY

Previous to these developments, polyvinyl ether (PVE) was selected as the most suitable refrigerant oil for HFC's [2]. And the applications of bronze metal for journal bearings and Si-rich aluminum alloy for oldham coupling were recommended to prevent seizing and large wear of sliding parts.[2]

Therefore, these modifications can prevent the peculiar lubrication troubles when using R407C. The accelerated endurance tests(*1) and the life endurance tests(*2) were carried out for use with R407C and PVE. The reliability of the developed compressor has already been verified.

(*1) tests for the verification of part strength by loading extremely large stress.

(*2) tests for the verification of part life by loading larger stress than normal conditions.

The results of these endurance tests and the evaluation of sliding materials for R407C are shown in Table 1.

In addition, It have been confirmed that the above mentioned improvements in the sliding parts are also applicable for R410A in the endurance tests.

IMPROVEMENT OF COP

Previous to these developments, the pressure of a cylinder in compression process was measured by using the conventional scroll compressor (for use with R22) in order

to analyze the indicated loss when using R407C with PVE. Fig.2 shows an example of P-V diagram. This diagram shows the items of indicated loss, or the over-compression loss, the leakage loss, the heating loss, and the under-compression (re-expansion) loss.

Table 2 shows the indicated loss of R407C and its items when the conventional scroll compressor is used. The indicated loss of R407C is larger than that of R22. The increase in over-compression loss of R407C is little, but the other losses (leakage, heating, under-compression) are larger than those of R22. As for leakage loss, this loss would not increase since the viscosity of PVE is higher than that of mineral oil. As for heating loss, it would not also increase because of the lower temperature of R407C compared with R22.

Therefore, the primary cause of increase in the indicated loss is due to the increase of under-compression loss because of the higher pressure ratio of R407C compared with R22.

First, the design compression ratio of the scroll was increased in order to adapt for the pressure increase associated with using R407C. And second, the shape of scroll center was changed to reduce the over-compression loss to obtain more COP.

Fig.3 shows the shape of the newly designed scroll center and that of conventional scroll center.

As a result of these approaches, the newly designed scroll gained about 3% improvement of COP.

OIL CIRCULATION

It is an important problem to reduce the refrigerant oil discharged into a system from a compressor with refrigerant gas from the following points of view ; the reliability of compressor and the efficiency of system. So, in the higher pressure chamber, the oil mist were separated from discharge gas by using the rolls of fine wire net (referred to as demister hereafter), and the separated oil were returned to lower pressure chamber through an oil return tube, as shown in fig.4.

However, the oil circulation ratio(*3) of PVE used with R407C is over two times lager than that of mineral oil used with R22.

(*3) weight percent ratio of the oil contained in the refrigerant in the system.

As a result of the investigation of this phenomenon, it was found that the less wettability of PVE due to the lager polarity of PVE in its molecular than that of mineral oil is the cause of the increase in the oil circulation ratio. That is to say, the polarities of PVE and POE (polyol ester) are very strong because these oils contain oxygen radical

in their molecular structures ,which makes PVE and POE miscible with HFC's. So that, the initial mono molecular films of PVE on the surface of a demister, caused by its strong polarity, repel mists of PVE when PVE touch on the surface of the demister in succession.

Therefore, the demister, which has dimples on its surface to improve the wettability with PVE, was applied and succeeded in reduction of oil circulation ratio by about 70% in case of R407C and PVE.

Fig.5 shows the photographs of the dimples. Table 3 shows the effects of the improved demister. The treatment of these dimples is done by blowing hard particles such as Al_2O_3 and SiO_2 on the surface of fine wire net. So, the improved demister is not expensive and high efficiency.

As for these dimples, some reports have suggested the following effects.[3) 4) 5)]

i) Chance of adsorbing the oil mists can increase because the surface area of demister is larger because of the dimples.

ii) The oil mist can be interlocked in the micro-cracks made on the surface.

iii) The reactive surface that have many lattice defects, or lattice deformations and dislocations, can get high adsorbility of the oil mists.

iv) Due to the exoelectron phenomenon (Kramereffect[6)]) that has not been made clear, electron emission from the surface that have dimples makes the surface reactive.

【CONCLUSIONS】

The above mentioned modifications could solve the decline in reliability, COP reduction , and increase in oil circulation, when used with R407C, which led to success in developing the series of new compressors for R407C. In addition, it was confirmed that these modifications were also applicable for R410A.

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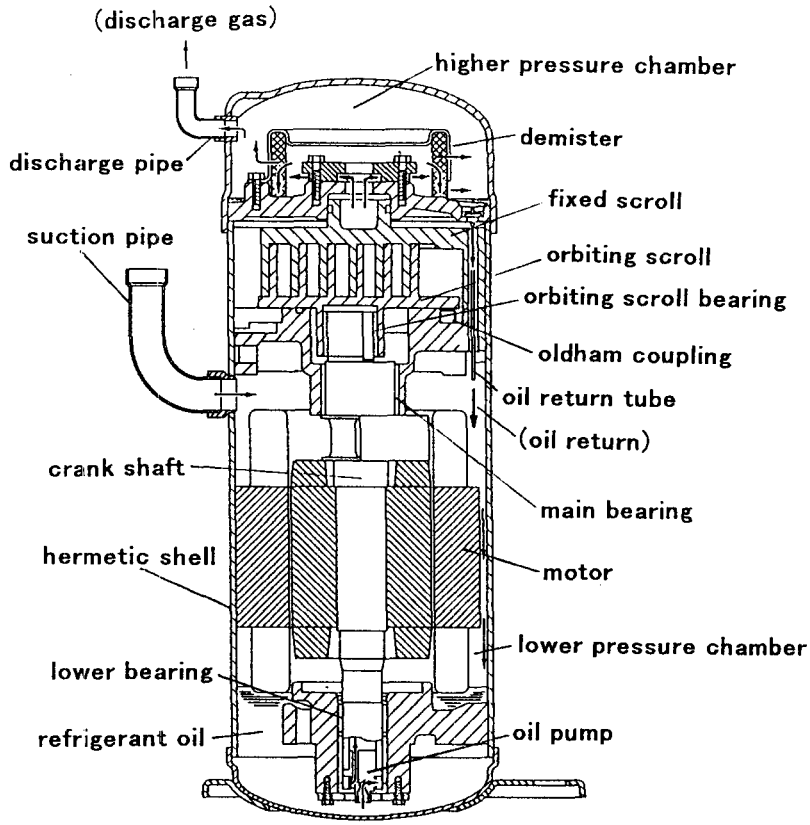

Fig. 1 Section of developed compressor

Table 1. Results of compressor endurance tests and evaluation of sliding materials for R407C

sliding parts	materials	compressor endurance tests		evaluation of sliding materials*1)	
		wear amount ratio*2)	seizing	wear amount ratio*1)	seizure load ratio*3)
bearing metal	aluminum alloy (conventional)	—	seized	1.0	1.0
	lead bronze (modified)	—	not seized	0.25	1.33
oldham coupling	silicon aluminum alloy (conventional)	1.0	—	1.0	—
	silicon-rich aluminum alloy (modified)	0.1	—	under 0.02	—

*1) from S.Hiodoshi et al "Evaluation of refrigerant oil and sliding materials for alternative refrigerant", 1997 International Conference On Ozne Protection Technologies

*2) the wear amount ratio = (wear amount of modified materials/wear amount of conventional materials,under R407C)

*3) the seizure load ratio = (seizure load of modified materials/seizure load of conventional materials,under R407C)

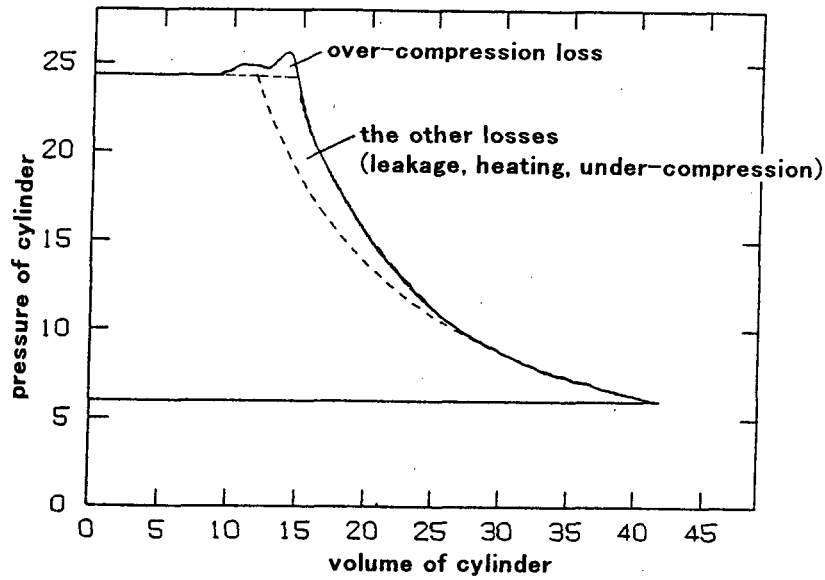

Fig. 2 P-V Diagram

Table 2 the items of indicated losses of conventional scroll compressor

ratio of indicated loss*2)	ratio of over-compression loss	ratio of the other indicated loss*3)
110	101	111

*1) test condition : ratio of operation pressures=4.06
;(higher pressure/lower pressure=4.06)
test frequency=60Hz
*2) ratio of each losses=(loss of R407C/loss of R22)×100
*3) losses of the leakage, the heating,
and under-compression (re-expansion)

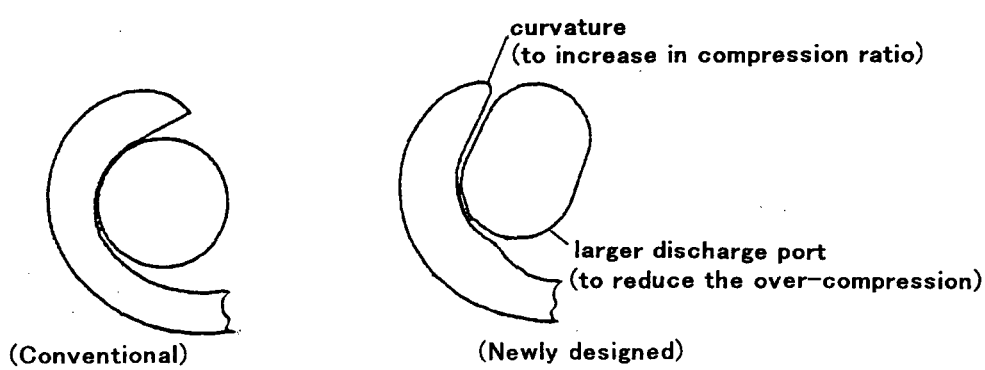

Fig. 3 Shape of newly designed scroll center

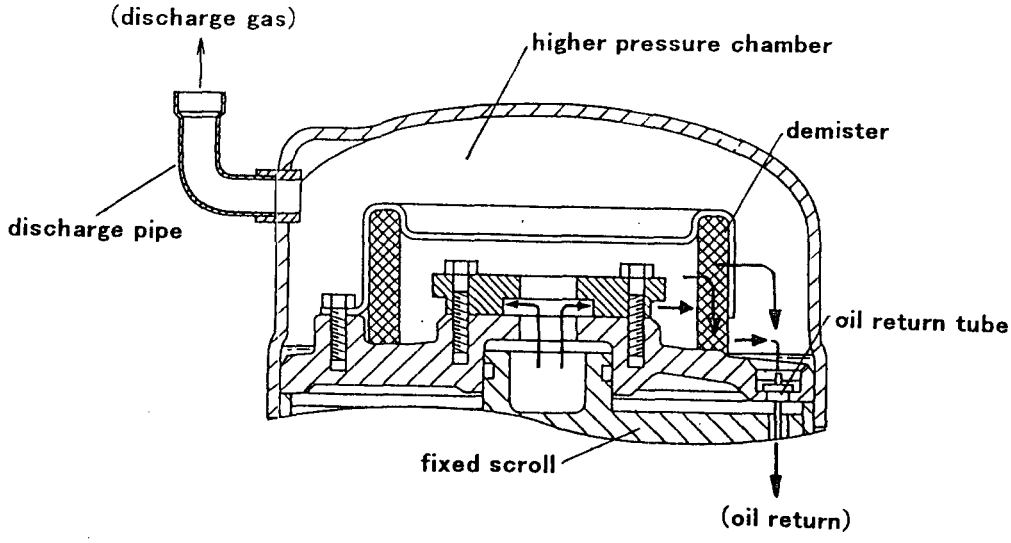

Fig. 4 Structure of oil separation

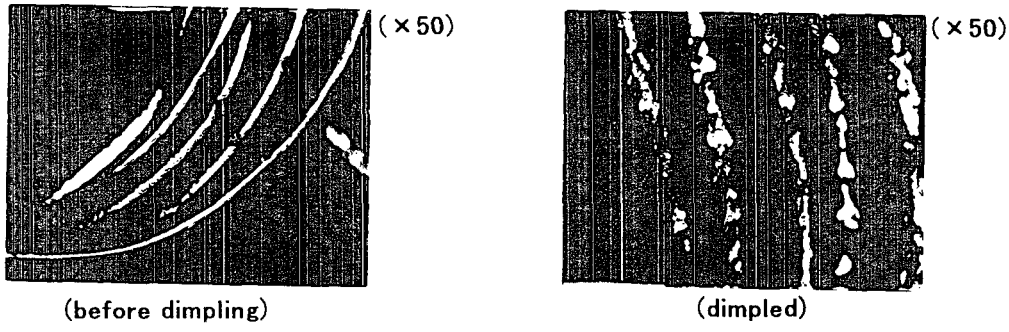

Fig. 5 Photographs of dimples on demister

Table 3 Effect of the improved demister

demister	ratio of oil circulation*1)	efficiency of oil separation[%]*2)
conventional	100	80
improved (dimpled)	33	93

*1) ratio of oil circulation
= (amount of oil circulation for using improved demister / that for using conventional demister)

*2) efficiency of oil separation ; percentage of separated oil mists by using the demister in the higher pressure chamber

Comparative Life Cycle Testing of Hermetic Compressors with CFC-12 and HC-blend

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INTRODUCTION

The life cycle test is conducted on a hermetic compressor to study the chemical and material compatibility of parts exposed to refrigerant and oil. The object of the test is to obtain, for a given compressor, in a relatively short time, a representation of its reliability after a long period. It takes into consideration the behaviour of materials in the compressor in the presence of refrigerant and oil at relatively high temperature and pressure.

The Research centre for Refrigeration and Heat pumps Ltd. (FKW), in collaboration with the University of Hannover, Germany has developed a special test rig and procedure for assessing the compatibility of materials and components of a hermetic compressor with a combination of refrigerant and lubricating oil. Unlike the traditional test methods, the test method developed by FKW is intended to compare the well known combination of CFC-12 and mineral oil with other refrigerant-lubricant combination, e.g. hydrocarbon mixture and mineral oil or HFC refrigerant with ester based lubricants. It appears that most of the standards, including DIN, were developed for testing the compressor with an oil sample and one refrigerant and not as a comparison test. The values of saturation pressures chosen by the DIN standards are mainly taken for refrigerant CFC-12. The discharge pressures of HCFC-22 and R-502 are too high to perform tests with 70°C or 90°C condensing temperatures. The standards have not yet been updated for refrigerants like HFC-134a , isobutane and blends.

To make a comparison between different oil types and refrigerants, it is necessary to run the tests under identical pressure and temperature conditions. Investigations to determine the quality of different oils can be made once the principal selection of the refrigerant is determined.

LIFE TEST CYCLE TESTS

LIFE CYCLE TEST RIG : The test rig employs a simplified gas cycle without evaporation and condensation of the refrigerant. The cycle involves the compression of superheated vapour from a specified suction pressure to a fixed discharge pressure. The cooling process is just a desuperheating process. The refrigerant still in the superheated vapour region is expanded to the suction pressure through an expansion valve. The refrigerant is then recycled by the compressor from low pressure to high pressure. The operating pressures are determined by the quantity of the refrigerant charge and the expansion valve adjustment. The expansion valve is adjusted manually to achieve the desired suction pressure. If the discharge pressure is higher than the required pressure, a hand valve provided in the charging line is used to release the extra quantity of refrigerant charged. These required conditions are obtained by a trial and error procedure.

The test rig consists of the hermetic compressor to be tested, a muffler or buffer, a cooling coil,

an automatic expansion valve. The muffler or buffer is provided after the compressor to accommodate any excess quantity of refrigerant. The suction pressure is controlled by a spring loaded automatic expansion valve. The test circuit is maintained at a constant temperature, e.g. 50°C. The heat of compression may partially or fully provide the heat required to maintain the high temperature ambient temperature. Two fans have been fitted to the housing. A heater, connected to a temperature controller, is placed at the bottom of the compressor. The suction fan takes fresh outside air into the instrumentation compartment and then it supplies this air into the housing to maintain the ambient temperature. The temperature inside the housing can be controlled by varying the speed of the exhaust fan fitted to the back of the housing. The test rig consists of all necessary control, monitoring and measuring devices, to run with a hermetic compressor up to three ampere current.

The respective temperatures of state points such as suction, discharge, ambient and oil temperatures, the current drawn by the compressor, can be monitored on the control panel. The speed of the fan can be controlled to maintain the ambient temperature inside the housing. The run time of the system is measured by the timer on the control panel.

To measure the temperature at various state points, temperature sensors are kept in small copper tubes brazed on to the test circuit at the appropriate place. The ambient temperature is sensed by keeping the temperature probes in the middle of the test circuit or housing. To ensure the accuracy of temperature measurement at suction and discharge connections, the thermal insulation tapes are wound over the temperature probes.

PREPARATION OF THE TEST RIG : If the test is to be carried out on a new hermetic compressor, it is cut open, before the test. While cutting the compressor, care is taken to prevent any entry of cutting metal particles into the compressor shell. Otherwise, it may affect the cylinder surface, piston skirt, reed valve or valve plate surfaces. After cutting the compressor, it is dismantled according to the assembling order. During the dismantling process, the gaskets on both sides of the valve plate are removed so that matching surfaces are not damaged. The compressor parts like piston, crank case, connecting rod, etc. may be cleaned with the lubricating oil used in the compressor. The well-cleaned compressor parts are visually checked for any damage to the surface; if anything abnormal is observed, it is noted down for comparison after the test. The compressor parts are then cleaned with a dry cloth and finally by using a jet of air to remove any adhering particles. Photographs of all the parts such as piston, valve plate, cylinder head and crank case of the compressor in close-up are taken as a record. After visual inspection and photographing, the parts are again washed in the recommended lubricating oil and reassembled accordingly. While reassembling, instead of the original gaskets, new gaskets may preferably be used. Before tightening the valve plate and cylinder head over the crank case, the clearance volume must be checked by revolving the crank shaft.

The properly assembled compressor is then welded to make it hermetically sealed. While welding the compressor shell, care should be taken to avoid the entry of any metal particle or burned carbon particles inside the shell. The leak test of the compressor is made by fully immersing it in water also making sure that there is no entry of water inside the shell. Then the compressor is run on air to check whether the compressor is able to achieve compression.

Small copper tubes are brazed over the suction and discharge side of the compressor for

temperature measuring probes. Similarly, a tube is also brazed at the bottom of the compressor for the probe to measure the oil temperature inside the compressor shell. Besides the type of oil and the refrigerant to be tested, it is important to use the right solvent to clean the tubes. Petroleum ether was used in this study.

The compressor, after leak test at normal pressure, is fitted to the test circuit. Leak test at higher pressure, suitable for piping and joints, is then carried out using nitrogen gas at a pressure of nine bar. The expansion valve must be kept widely opened and the hand valve on the charging line fully closed, while taking the leak test. Before placing the platform into the housing, the test rig is evacuated via the charging line provided in the test circuit for five hours. The appropriate quantity of lubricating oil, as recommended by the compressor manufacturer, is charged by breaking the vacuum.

Charging of CFC-12 to the compressor is easier as compared to hydrocarbon refrigerant mixtures. Before charging, the expansion valve is kept fully open and the hand valve fully close. After purging with a small quantity of gas through the charging line, the hand valve is opened gradually. When the pressures are about 2-3 bar, the hand valve is fully closed and the charging line is disconnected. The test platform is slid into the housing and the test unit is put on. The suction and discharge pressures are allowed to stabilize for some time. The expansion valve, which is initially kept fully open during the charging, is slowly closed to set the suction pressure at 2.2 bar. As the run proceeds, the temperature inside the rig and the housing will gradually rise which will result in the increase of the discharge pressure. If the discharge goes beyond the recommended value (18.5 bar in this study), then some quantity of refrigerant may be vented, by a gradual opening of the hand valve, to maintain the discharge pressure at the desired level. The suction pressure should be monitored. If it is varying, readjustment of the expansion valve is done. If the unit gets overcharged and pressure exceeds the set point, say 25 bar, the compressor will trip. In the same way, undercharging should also be avoided. This is shown by the fact that the discharge pressure does not increase as the compressor warms up. This procedure is continued till the pressures reach the desired value and the temperature inside the housing reaches 50°C.

The hydrocarbon mixture is charged differently. The charging of this refrigerant being a mixture, is done in the liquid form rather in the gas form. Since this is a flammable refrigerant, safety measures play a prime role while charging. For cylinders without a dip tube, as is the case with many small cylinders, a specially made charging line (coil type having a length of about 0.5m) is connected to the refrigerant cylinder with an adopter. The cylinder is kept in an inverted position to ensure that there is no change in the composition of the refrigerant as it is being charged. The refrigerant slowly vaporises as it passes through the coil and finally gets charged as gas with the same composition. Care must be taken with the hydrocarbon refrigerants that there are no loose electrical connections in the circuit to avoid any sparks.

EXPERIMENTAL TRIALS : In this life cycle testing the run time was 2000 h. Before dismounting the compressor after the test, the lubricating oil was drained and saved in a dry and air tight bottle. The dismounted compressor shell was then cut open. Care was taken while cutting to avoid any particles entering the compressor. Also, photographs of the parts of the compressor were taken. Comparison of the compressor parts before the test and after the test was done. The visual observations of the compressor parts were entered in the visual rating tables.

The wear effects of these parts were measured by using perthography. Analysis of the lubricating oil samples, before and after the test, was carried out for both the test samples. The oil samples were examined for the following: (i) Water Content by Karl Fischer test, (ii) Chloride ion content by selective ion electrode analysis, (iii) Acidity of oil (Total Acidity Number) by KOH titration, (iv) Metal content by IR spectroscopy, (v) Chemical decomposition by NMR spectroscopy, (vi) Viscosity by Ferranti Shirley Viscometer

RESULTS AND DISCUSSIONS

Two compressors, one (Compressor A) with CFC-12, to establish the benchmark data, and the other (Compressor B) with HC mixture (DIN Grade with 99.95% purity), were tested. After dismantling the compressor, the first step taken was the visual observation of the compressor parts. The compressor and various components were individually inspected for any notable damage to materials, e.g. abnormal metal wear, degradation of polymeric materials and for thermal and chemical effects. The parts were also observed for reaction products such as sludge, tar and coke.

Compressor A : Inside of the compressor A had turned faint brown. The drained lubricating oil was reddish brown and it appeared to have become more viscous. The lubricating oil had some floating particles on the sides of the housing. These floating particles may be due to sludge or metal wear. The insulating plastics strips on the motor winding had become hard after the test.

On the cylinder head i. e. on suction and discharge sides, there was some sludge formation. The layer was uniform on both the sides. In these chambers, there was no indication of the corrosion or copper plating. The surface of the cylinder or bore showed some traces of sludge, lacquer and thermal effect. There was an indication of the wear and it was seen clearly on the perthographs of the cylinder surface to be discussed later.

Like the sludge on the cylinder suction chamber, the suction side valve plate also had a similar coating. As per the visual rating, there was ample lacquer on the valve plate. Both the surfaces of valve plate were not affected by any corrosion. The same was observed on the valve plate discharge and cylinder sides. Thus valve plate as a whole had only lacquer and sludge as a major change and there was no corrosion or copper plating. The suction valve pivoted on the valve plate and the discharge valve had also a deposit of sludge layer along with lacquer and the sludge formation was uniform.

Another important part of the compressor i.e. piston had its top portion had become black. It showed a uniform layer of blackish colour. The insulation lacquer deposit was in large scale and it had equal effect on the piston side as well. The lateral surface of the piston had some wear impressions. Visually this wear impressions indicated low wear in the rating scale. Crank shaft showed some copper plating. The copper plating was concentrated on the surface of the crank shaft facing towards piston i.e. upper surface. The lacquer and wear of the crank shaft surface were significant and both effects were on the same side as that of copper plating. It is because, during the movement of the piston from the bottom dead centre to the top dead centre, the crank shaft requires more power to compress the refrigerant and hence the force transmitting surface is the surface facing the piston. At the same time, the effect of the same movement is on the piston pin. The piston pin had more wear rating in the unacceptable range. The copper plating and

lacquer had the same rating as that of wear. The sludge was in the middle range. All these effects were on the surface of the piston pin facing towards the piston. Thus, of all the parts, only crank shaft and piston pin showed the effects of three criteria.

As per the various individual ratings, the individual summary ratings may be obtained. Copper plating had come to the visual rating of 2 and it is very small. Hence after testing the hermetic compressor with CFC-12 , it can be considered that the Compressor A had no considerable adverse effect of copper plating. The compressor was mostly affected by the lacquer and sludge having rating of 5 each. The individual summary of the corrosion showed that there was no parts corroded and hence the zero rating. The average wear effect had come to be 4 and which is in the middle rating scale. This global summary of the visual rating is the base line for comparison for Compressor B visual ratings and global summary.

Compressor B : The housing of the compressor did not show any sludge or corrosion over the surface. The drained lubricating oil appeared slightly dark brown colour with no floating particles. The oil in this test was not as much viscous as it was in the previous case. The upper compressor shell was very clean and there was no change in colour. There was no trace of the sludge over the winding of the stator. The insulating plastics strips were not as hard as in the earlier case and exhibited the flexibility.

The cylinder head suction side as well as the discharge chamber had sludge in traces but by comparison, both were clean. These chambers had no lacquer and corrosion on the inside surfaces. The surface of the cylinder was very clean with no traces of sludge. However it showed some wear impressions on the surface. On the valve plate suction side, there was no sludge but it was in traces on the discharge side indicated by blackish shade. Also the cylinder side of the valve plate had turned faint black which was the indication of the sludge in traces. The lacquer and sludge, the only effects on the above parts and the sides, were negligible, compared to Compressor A. The suction and discharge valve had turned light brown, with the lacquer in traces but no sludge. Hence these valves were very clean compared to the heavy sludge in Compressor A.

The piston head of the Compressor B was comparatively clean. There was a very light shade of black colour. The piston at the side or the piston skirt was also very clean with comparatively less wear impressions. Also there were no copper plating or lacquer and sludge coatings on its surface. In the case of crank shaft, the copper plating and wear of the surface facing the piston were in the lower range of the visual rating. Comparatively, the copper plating on the crank shaft was less than that of Compressor B. Copper plating appeared on the piston pins (top side) with wear impressions while the remaining criteria were nil.

As the copper plating had no effect on all the compressor parts except the piston pin, it was considered to be zero in the case of Compressor B. The rating for lacquer had come to an average of 2 in the visual rating. Thus lacquer on the parts was in traces and comparatively negligible. The sludge formation was also in traces. The sludge in the previous case was in large scale whereas here it was zero by comparison. Like Compressor A, in this compressor too, there was no corrosion of any parts and by rating scale, it had come to zero.

The friction between surfaces results in wear of metal. Only parts like piston, piston pin, cylinder

and crank shaft had a wear rating of 2 which is considered to be in the lower range. The individual summary of all the criteria lies between 1 and 2. This means that the key factors are well below the base line ratings for Compressor A.

With low ratings of the individual summary, the global effect of all these parameters is naturally low and the final rating is 2. By comparing the global summaries of visual rating results of both compressors, evidently the compatibility of the compressor parts with the alternative refrigerant HC-290/HC-600a, using the same mineral oil, is better than with CFC-12.

SURFACE FINISH MEASUREMENTS :The cylinder, piston, and piston pin were tested by using perthography for surface roughness before and after the test. For cylinder and piston, both sides were tested whereas the piston pin was tested on its outside surface facing the piston. The perthography measurements for Compressor A revealed that there was no considerable wear over the surfaces of cylinder and piston. The measurements for the piston pin showed considerable changes and are the indication of maximum wear of the surface. The piston pin had undergone a change in its diameter after the test by 0.02 mm; the change in its average roughness value is 0.967 μm. There were no considerable wears on the cylinder and piston of Compressor A observed.

The surface finish measurements of the cylinder, piston and piston pin of Compressor B, showed very little difference in the roughness values, before and after the test. It was observed that these values were less than the values obtained for Compressor A and therefore, suggest comparatively negligible wear. There were no observable changes in the diameters of the piston, excenter and piston pin. Thus it can be concluded that there was no adverse effect of the HC mixture and mineral oil combination on the metallic moving parts of the compressor.

OIL SAMPLE RESULTS : The oil samples taken after the tests were analysed for water content, total acid number, chloride content, metal content, chemical degradation. The viscosity of tests samples were also measured.

Water Content : The water contents of lubricating oil samples, before and after the test, were measured by using Karl Fisher Titrator. The results are presented in Table 1.

TABLE 1 : WATER CONTENT OF OIL SAMPLES

Sr.No.	Compressor/Refrigerant/Oil	Water Content (ppm)
1	Mineral oil (before test)	118
2	Compressor A/ CFC-12/ Mineral Oil (after test)	110
3	Compressor B/ HC-290/HC-600a/ Mineral Oil (after test)	154

From Table 1, it can be seen that the water content of the mineral oil before the test was 118 ppm. In the case of Compressor A tested with CFC-12, the water content had marginally

decreased to 110 ppm. While the lubricating oil in Compressor B tested with the hydrocarbon blend, the water content had increased to 154 ppm. All these samples were not subjected to any degassing or evacuation before analysing for the moisture content. The increase in the water content cannot be explained by any logic.

Total Acid Number : The total acid number of the three oil samples were measured by KOH Titration. The results are presented in Table 2.

TABLE 2 : ACIDITY OF OIL SAMPLES

Sr.No.	Compressor/Refrigerant/Oil	Acidity (TAN)
1	Mineral oil (before test)	0.068
2	Compressor A/ CFC-12/ Mineral oil (after test)	0.131
3	Compressor B/ HC-290/HC-600a/ Mineral oil (after test)	0.0623

The total acid number of the lubricating oil from Compressor A tested with CFC-12 had increased from 0.068 to 0.131 after the test. However, for the HC mixture, the acidity of the oil after the test was quite similar as that of the original oil. It is a clear indication that, with lower acid formation with the HC mixture, copper plating and other sludge formation will also be much lower.

Chloride Ion Content : The test for the chloride ion in the lubricating oil was done, using the Calomel electrode system with a Chemita Ph/Potentiometer. As to be expected, in the mineral oil used in combination with the hydrocarbon blend in the Compressor B, there was no measurable chloride ion as in the case of the neat oil sample. This is to be expected as there is no chlorine atom present in the HC refrigerant. The chloride ion present in the oil sample from Compressor A tested with CFC-12 was less than 10 ppm, which is within the limits of measurement. Therefore, obviously there was no acid formation due to any chemical reaction between CFC-12 and the mineral oil. However, there is a distinct advantage with the HC mixture as there is absolutely no possibility of any acid formation because of the absence of chlorine in the fluid combination.

Metal Content : For the analysis of metal in the mineral oil before and after the test, the instrument used, was Chemita Model 203, Atomic Absorption / Emission Spectrophotometer. The metal analysis showed that the contents of iron, copper and aluminium in the oil, before and after the test, were less than 1 ppm; this can be considered negligible. It means there is very low wear of the parts of the compressor to show any measurable metal content in the oil.

Viscosity : The viscosity of the oil samples was checked before and after the test because it suggests the decomposition and reaction, if any, taking place during the test. This measurement was done in the Polymer Processing Centre at NCL, using the Ferranti-Shirley Cone and Plate Viscometer. The tested oil samples were degassed at 80°C in a vacuum and the measurements

were repeated. The viscosity data are presented in Table 3.

TABLE 3 : VISCOSITY OF OIL SAMPLES

Sr. No.	Compressor/Refrigerant/Oil	Viscosity (cp)
1	Mineral oil (before test)	~ 56.00
2	Compressor A/ CFC-12/ Mineral oil (after test)	~ 50.00
3	Compressor B/ HC-290/HC-600a/ Mineral oil (after test)	~ 50.00

For both compressors, the viscosities of the lubricating oils, after the test, had decreased. The viscosity of the oil before the test was approximately 56.0 cp and it had come down to 50 cp after the test, in both the compressors. The decrease in viscosity could be due to dissolved refrigerant in the oil. The tested oil samples were degassed under 80°C and vacuum. It is still possible that there were still traces of the refrigerant and this could very well reduce the viscosity. It can only be concluded that there was no chemical reaction, therefore, no change in the viscosity.

Chemical Decomposition and Reactions : The structural analysis of the oil samples before and after the test suggests the reactions between the oil and refrigerant. Therefore, the mineral oil samples were analysed by using the Fourier Transform Infrared (FT-IR) Spectrophotometry and Proton Nuclear Magnetic Resonance (NMR).

FT-IR Spectrophotometry of the oil was done by using Perkin- Elmer 16 PC . The FT-IR spectrometry of the mineral oil samples showed that there was no change in the chemical structure of the oil after both tests. However, there were indications to suggest the formation of organic acids in very small concentrations. These organic acids are not as reactive as the inorganic acids like hydrochloric acid. A few other modifications of the original chemical structure could be observed but in a negligible order. Thus, the interpretation of the FT-IRs of the oil samples showed no considerable degradation of the oil in both the cases.

Nuclear Magnetic Resonance of the oil samples was carried out by using Perkin Elmer AC-200. Similar to the FT-IR results, the NMR analysis of all the three samples also suggested that there was no chemical degradation of the oil in both the tests.

CONCLUSION

The summary of the visual observations showed that compressor tested with the HC mixture was clean; there was not much wear and sludge formation as with the CFC-12 compressor. From the perthograph results, comparatively there was no wear of the piston, piston pin and cylinder of the compressor tested with HC mixture. Only piston pin of the CFC-12 compressor had more wear.

The water content of oil tested with the hydrocarbon mixture was well below that from the CFC-12 compressor and this is considered an advantage. While the total acid number remains the same

for the oil tested with the HC mixture, it increased for the oil tested with CFC-12. It appears that there can be no chemical reaction between the HC mixture and mineral oil. The chloride ion and metal contents in the oil samples after the test were less than 10 ppm and 1 ppm respectively. From this result it may be concluded that there were no reaction and no significant wear of the parts of both the compressors. The viscosity of oil in both the compressors remained the same. From this, it can only be concluded that there was no chemical reaction leading to any polymerisation and therefore no increase in the viscosity. In the test for chemical decomposition and reactions, there was no measurable formation of any new chemical group; therefore, no chemical degradation of the oil had occurred.

From above results, it can be concluded that he hydrocarbon mixture is better compatible with the hermetic compressor materials than with CFC-12 even under retrofit conditions. This gives an opportunity to retrofit appliances with the HC mixture without any concern for stability except for safety due to flammability of the HC mixture.

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Field Testing of CFC-Free, Energy-Efficient Refrigerators in China

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Abstract

This article reports on the results of a year-long field test of prototype CFC-free, energy-efficient refrigerators developed during the Sino-US CFC-Free, Energy-Efficient Refrigerator Project. In early 1995, 104 refrigerators—85 prototypes and 19 baseline units—were installed in households in Beijing, Shanghai and Guangzhou. Watt-hour meters were installed to monitor energy usage, and the families were asked to respond to two questionnaires involving ownership and use of other appliances, satisfaction with the new and old refrigerators, rating of refrigerator characteristics, and other socio-economic information. Statistical analysis was performed on the energy consumption data along with the socio-economic information. Results show that laboratory measurements of prototype energy consumption closely match field energy consumption results in Shanghai, while energy consumption in Beijing and Guangzhou was lower for both the prototype and baseline models, with savings ranging from 22% in Beijing to 35% in Shanghai. Variables with important influence on energy consumption include model type, city, income level, and existence of kitchen fans and air conditioning. Except for noise levels, the prototypes generally received high consumer satisfaction ratings.

1. Introduction

The Sino-US CFC-Free, Energy-Efficient Refrigerator Project was initiated in 1989. The project was undertaken as part of a formal agreement between the China National Environmental Protection Agency (NEPA) and the US Environmental Protection Agency (USEPA) to reduce the usage of CFCs and improved the energy efficiency of domestic refrigerators within China. The initial stage of the project involved the development of a CFC-free, energy-efficient refrigerator design that has been thoroughly tested for reliability, performance and safety. This effort included the testing of a large number of models with different refrigerants and foam-blowing agents, advanced refrigeration cycles, thicker insulation, and other energy saving technologies.

The second stage of the project involved the conversion of a demonstration refrigerator production line at a factory to batch production of the prototype model developed in the first stage. This model included the following features selected from the many alternatives tested:

- Dual-evaporator, single-compressor vapor compression cycle with a valve directing the flow of the refrigerant through both evaporators or the freezer evaporator only
- Isobutane refrigerant
- Americold HC-77 1.43-COP high-efficiency compressor
- Ten percent larger wire-tube type freezer evaporator
- Wire-tube type condenser
- Cyclopentane-blown foam insulation, increased by 23 mm on the sides, back, and bottom, and 15 mm in the door
- Improved gasket

2. Field Testing

Field testing of the prototypes was crucial to demonstrating the safety and reliability of the CFC-free, energy-efficient prototype design. Moreover, it was important to determine how the energy savings of the

prototype in daily home use compared to the results of laboratory testing. Given multiple door openings throughout the day, food loads in the freezer and fresh-food compartments, and widely varying indoor temperatures throughout the year, energy consumption in actual household use would be expected to increase for both baseline and prototype units, reducing the relative savings. What is important to the future growth of electricity demand in China, however, is the potential for absolute savings relative to the baseline model.

The field testing program was designed initially to include all 200 of the manufactured prototypes, but about half the models were redirected before shipment to the three cities for testing. The field test period was set at one year, in order to capture the effect of all four seasons on refrigerator performance. Field testing took place in Beijing, Shanghai, and Guangzhou. The selected cities are large urban centers, with a substantial base of "middle class" consumers and about 100 percent refrigerator penetration in the urban market.

The three cities are indicative of three of China's major climate zones. Beijing, in North China, has a temperate climate characterized by hot wet summers and cold, dry winters. The annual average temperature is 12.9°C, with wide annual variations. The permanent population (i.e., excluding migrant workers) was 10.7 million at the end of 1995. Shanghai, at the mouth of the Yangzi River on the East China Sea, has a temperate climate characterized by hot wet summers and mild winters. The annual average temperature is 16.5°C, and the temperature usually remains above freezing during the winter. Shanghai is China's largest city, with population of 13.01 million at the end of 1995. Guangzhou, capital of the southern province of Guangdong, has a sub-tropical climate averaging 22.5°C in temperature annually. The summers are hot and wet, and winter warm. Guangzhou had 6.47 million inhabitants at the end of 1995. (SSB 1996)

3. Methodology

About 30 typical households were selected in each city to participate in the field test program out of a pool of about 60 households per city identified as possible participants. Participants were offered a prototype or baseline model refrigerator at a substantial discount to the market price. In addition, the households were offered regular payments during each stage of the program. All field test units were placed in the same part of each city to facilitate data collection.

In May and June, 1995, a total of 85 CFC-free, energy-efficient prototype units—model BCD-222B—and 19 baseline units—model BCD-225—were installed in the participating households. Incomplete energy consumption data were collected for four prototypes and five baseline units in Guangzhou. In addition, one prototype refrigerator failed and was dropped from the field test in Shanghai. Table 1 shows the locations of the remaining 94 field test units and the dates over which energy consumption readings were made.

At the time of the refrigerator installation, a watt-hour meter was also installed on all units to monitor energy usage. Readings of cumulative power consumption were made weekly for two months, and then monthly for the remainder of the roughly year-long field test program. A questionnaire designed to gather relevant socio-economic data such as household size, income, ownership of other appliances and usage patterns was administered one month into the test period. In addition, a second questionnaire concerning the customer's opinion about the prototype refrigerator was given at the end of the test period.

4. Characterization of Study Households

As part of the study, data were collected on the study households, old refrigerators, ownership and use of other appliances, and how households used their new refrigerators. These data were collected through

Table 1. Locations and Dates of Field Tests

City	Number of Units in Test	Test Dates
Beijing		
Prototype units	27	7/2/95 to 6/29/96
Baseline units	7	7/2/95 to 6/29/96
Guangzhou		
Prototype units	18	7/5/95 to 1/22/96
Baseline units	2	7/5/95 to 1/22/96
Shanghai		
Prototype units	35	6/25/95 to 6/20/96
Baseline units	5	6/25/95 to 6/20/96

questionnaires administered near the beginning and end of the study period to better understand household characteristics and how variations in household characteristics may affect refrigerator energy use.

Study Households

Households in the study had an average size of 3.1 people, with the average slightly higher in Beijing and slightly lower in Shanghai and Guangzhou. For China's urban areas as a whole, the average household size was 3.23 in 1995, down slightly from 3.28 in 1994 (SSB 1996).

Nearly half the households in our study has a monthly income as of mid-1995 between RMB 1001-1500 (about US$120-180), with about one-quarter having lower incomes and one-quarter having larger incomes. This income level of half of the respondents places them within the range of medium and medium-to-high income levels in urban areas (third and fourth quintiles). In 1995, the average monthly income per household in China's largest cities reached RMB 1407 (about US$170).

Old Refrigerators

All of the households in the study already owned refrigerators. Nearly all of these refrigerators were smaller than the new prototype model, averaging 165 liters (Table 2). The original units ranged in age from 2 to 20 years old, with the average unit being approximately eight years old, according to verbal reports by a member of each household. On average, the old refrigerator consumed 1.14 kWh/day, according to standardized testing information on the refrigerator nameplate. This is 36 percent more than the laboratory-tested consumption of the new prototype model. Thus, assuming these label measurements accurately portray consumption in the field, the average household could expect their new refrigerator to use 26 percent less energy than their previous unit. Old refrigerators were produced by more than a dozen

Table 2. Information on Old Refrigerators

Item	Average	Range	Number of Responses
Old refrigerator size	165 liters	100-220	41
Old refrigerator energy use	1.14 kWh/day	0.5-1.6	35
Year old refrigerator purchased	1987	1975-1993	40

manufacturers, with the largest number (nearly 30%) produced by Beijing-based Snowflake, formerly China's largest refrigerator manufacturer.

Ownership and Use of Other Appliances

Each of the households surveyed owned many types of appliances. Nearly all households had televisions and fans, and many had more than one. Around 70 percent of the households also owned clothes washers and microwave ovens. For the most part, ownership patterns are broadly consistent among cities, with the exception of space conditioning equipment. One-third of study households in Shanghai and Guangzhou owned air conditioners, while only 6 percent did in Beijing. Likewise, more than half of Shanghai households owned electric space heaters, because many apartments lack central heat despite average winter temperatures of approximately 6°C (43°F). In Guangzhou the climate is too warm generally to need space heating, while in Beijing all apartments have central heating.

As part of the survey, data were also collected on appliance nameplate power use and resident estimates of annual operating hours (broken down into days used per year and hours per day). Nameplate power use is typically a maximum load—average use is often substantially lower. Household estimates of operating hours are probably not very accurate. Also, for some of the appliances and cities, sample sizes were small and thus averages are biased by outliers. These data are summarized in Table 3. Particularly notable is the fact that residents report that on average televisions are operated 1235 hours per year, or over 3 hours per day on average.

Table 3. Information on Appliance Ownership and Operations in Study Households

Equipment Type	% of Households Possessing	Average Power (Watts)	Average Hours Used Per Year
Air conditioner	B: 6% S: 34% G: 33% Total: 24%	B: 800 S: 1172 G: 901 Total: 1040	B: 315 S: 328 G: 183 Total: 286
Washing machine	B: 73% S: 70% G: 63% Total: 69%	Total: 346	B: 123 S: 152 G: 199 Total: 159
Electric space heater	B: 3% S: 56% G: 0% Total: 22%	Total: 929	B: NA S: 259
Fan	B: 153% S: 143% G: 131% Total: 143%	Total: 103	B: 209 S: 426 G: 519 Total: 402

Equipment Type	% of Households Possessing	Average Power (Watts)	Average Hours Used Per Year
Rice cooker	B: 39% S: 52% G: 44% Total: 45%	Total: 659	Total: 343
Microwave oven	B: 70% S: 69% G: 56% Total: 65%	Total: 105	Total: 520
Kitchen exhaust fan	B: 12% S: 31% G: 0% Total: 16%	Total: 737	Total: 580
Television	B: 138% S: 124% G: 81% Total: 117%	Total: 103	Total: 1235

Note: B= Beijing; S=Shanghai; G=Guangzhou; Total = total of all three cities. Where individual values are not provided, values for individual cities were very similar to each other or sample sizes for individual cities were too small to be meaningful. Values greater than 100% indicate ownership of multiple units in households. Guangzhou data are derived from a small sample and may be biased. Guangzhou TV ownership may be biased downward, since no Guangzhou respondent answered the survey question about ownership of a second television.

Use of New Refrigerators

One month after the new refrigerator was installed, field staff visited each apartment and measured temperatures in the fresh food and freezer compartments using a mercury bulb thermometer. On average, they found that freezers were -17°C (+1°F) and fresh food compartments were 9°C (48°F). While Beijing temperatures were lower, temperature measurements were only made in a few Beijing homes, and thus these differences may not be significant. On average, both the fresh food and freezer compartments were approximately half full with food at the time of the field visit.

5. Field Test Energy Consumption Results

On completion of the field tests in June 1996, energy consumption results were compiled and combined with socio-economic data into one large data set, and a series of analyses of variance were performed. The results of these analyses are described below. The analyses were based on 85 observations of energy consumption with associated socio-economic information, since 9 more observations—one prototype in Beijing, one baseline in Guangzhou, and seven prototypes in Shanghai—contained more than 90 percent missing values and had to be deleted from the analyses. All analyses were performed with Statistical Analysis System (SAS) procedures Proc Ttest and Proc Glm.

Overall Energy Consumption

The two-sample t-test revealed that prototype refrigerators consumed on average 26.8 percent less energy than baseline refrigerators. This difference is significant, with the p-value less than .0001. This p-value indicates that there is only a .01 percent chance that the average energy consumption of the prototype re-

frigerators is the same as that of the baseline refrigerators. The 95 percent confidence interval for the energy savings of the prototypes is 21.5 to 32 percent.

Laboratory tests of the prototype model BCD-222B showed an average 39 percent reduction in energy use compared to the baseline BCD-220 model. Based on Chinese testing procedures (performed at an ambient temperature of 25 °C), the BCD-222B consumed 0.84 kWh per day, compared to 1.37 kWh per day for the BCD-220 model. The BCD-220 was, however, replaced by a new BCD-225 model at the time of the field testing program. About 5 percent more efficient than the 220, the 225 consumed 1.3 kWh per day (based on Chinese testing standards). With the BCD-225 as the baseline model, the prototype thus consumed 35% less energy in standard tests (Table 5).

Table 5. Mean Energy Consumption, kWh/day

Model	City	Mean	Sample Size
Prototype	Beijing	0.78	26
Prototype	Guangzhou	0.79	18
Prototype	Shanghai	0.84	28
Baseline	Beijing	1.00	7
Baseline	Guangzhou	1.10	1
Baseline	Shanghai	1.29	5

Relationship of Energy Consumption to Socio-Economic Factors

This analysis seeks to determine if the observed difference between the energy consumption of the prototypes and baselines can be explained by any of the socio-economic factors collected in the questionnaire. For example, if all prototype refrigerators happened to be installed in Beijing and all baseline models in Guangzhou, the difference in energy consumption could simply be due to the difference in temperature between the cities. Hence it is reasonable to examine the differences between models by city, income group, and other factors. Results for some of these pair-wise comparisons of prototypes and baselines are summarized in Tables 6 through 10.

Table 6. Energy Savings versus Location
n=85

City	Energy Savings	p-value	Conclusion	95% Confidence Interval for Energy Savings
Beijing	22%	.0001	Significant	(18.5%, 25.5%)
Guangzhou	28%	.0003	Significant	(20.8%, 35.3%)
Shanghai	34.7%	.0001	Significant	(32.1%, 37.2%)

Table 7. Energy Savings versus Family Income
n=84

Income Group	Energy Savings	p-value	Conclusion	95% Confidence Interval for Energy Savings
2	28.5%	.1203	Non-significant	
3	32.6%	.0009	Significant	(26.8%, 38.4%)
4	18.1%	.0001	Significant	(12.1%, 24.1%)
5	36.5%	.0001	Significant	

Table 8. Energy Savings versus Air Conditioning
n=84

A/C	Energy Savings	p-value	Conclusion	95% Confidence Interval for Energy Savings
No	24.7%	.0006	Significant	(17.7%, 31.7%)
Yes	30.6%	.0001	Significant	(24.7%, 36.5%)

Table 9. Energy Savings versus Electric Space Heater
n=84

Heater	Energy Savings	p-value	Conclusion	95% Confidence Interval for Energy Savings
No	25.5%	.0001	Significant	(19.8%, 31.3%)
Yes	34.0%	.0001	Significant	(29.7%, 38.3%)

Table 10. Energy Savings versus One Fan
n=80

One Fan	Energy Savings	p-value	Conclusion	95% Confidence Interval for Energy Savings
No	21.4%	.0009	Significant	
Yes	27.1%	.0001	Significant	(21.4%, 32.7%)

Table 6 indicates that geographical location is a significant indicator of prototype energy savings. The results shown in Tables 7 to 10 indicate that the prototype's energy savings is significant for these other variables as well. This implies that the observed difference in energy consumption can be explained by no single variable, other than that the prototype is more energy efficient than the baseline. (An insufficient number of complete data sets was available to do a step-wise analysis to determine if the energy consumption difference between the two models could be explained by a combination of two or more of the socio-economic factors.)

Tables 7 to 10 compared the energy consumption of the two models as a function of one of the socio-economic factors (e.g. city, family income, etc). The energy consumption of the baseline and prototype models in these comparisons was in most cases significantly different. It is also possible to look at one model and determine if its energy consumption is significantly affected by socio-economic factors. For example, looking separately at apartments with and without air conditioning, it can be ascertained if energy consumption of the prototypes and baseline models is significantly influenced by the presence of air conditioning. The result of this analysis shows that except for city temperature, the relationships between prototype energy consumption and the various socio-economic factors are not significant. Additionally, except for family income and number of inhabitants, the relationships for the baseline units are all significant. Thus the energy consumption of both refrigerators is strongly dependent on city temperature and independent of family income or family size.

Finally, an analysis for "important" variables affecting the energy consumption of all of the refrigerators indicates that the factors given in Table 11 have a significant effect on energy consumption:

Table 11. "Important" Variables Affecting Prototype Energy Consumption

Factor	p-value	Number of Observations Used in Analysis
Model type	.0001	85
City	.0001	85
Income	.0014	84
Kitchen fan	.0019	83
Air conditioning	.0035	84
Number of people	.0105	36
Two fans	.0480	80

It must however be noted that the significance of the effect of number of people in household on energy consumption is not as reliable as the other conclusions because the analysis is based on too few (i.e., 36) observations. Also, the p-value for Two Fans is close to .05, so this factor is likely insignificant.

Summary of Findings

Despite the limited size of the data set collected by the end of the field test period, several conclusions can be drawn about the operation of the prototype refrigerator in households. Clearly, the prototype refrigerator demonstrated substantial energy savings over the baseline model, averaging a reduction of 27 percent in power consumption. This compares to a 35 percent reduction in laboratory testing.

Greater savings were enjoyed in the warmer cities, with the lowest savings found in Beijing (22%) and the highest in Shanghai (35%). The lower savings in Beijing and Guangzhou were in part due to the unexpectedly low electricity use of the baseline refrigerators, which consumed on average 19 percent less power than in laboratory tests. Power use by the prototype refrigerators in these two cities also was about 7 percent less than in laboratory tests. In both cases, relative and absolute savings were lower than what was achieved in the laboratory. Interestingly, the consumption figures for Shanghai almost exactly matched laboratory tests for both the prototype and the baseline, resulting in comparable savings.

Households with space heaters showed higher energy savings than those without space heaters, as would be expected from refrigerators with thicker insulation. Some results, however, were counterintuitive, as higher savings were also demonstrated in households with air conditioners and kitchen exhaust fans.

Households with air conditioners achieved an average 34 percent reduction in refrigerator energy consumption compared to 26 percent for non air-conditioned households. Kitchen exhaust fans, which would also presumably reduce kitchen temperatures, also affected savings: in those households equipped with kitchen exhaust fans, savings increased by 6 percent.

Shanghai had the highest level of space heater ownership. The heaviest use of air conditioners was also in Shanghai, where both the power rating and number of hours of annual use were higher than in Beijing and Guangzhou (see Table 3). Shanghai led in terms of the number of households with kitchen exhaust fans, and the higher ownership of all three types of appliances may in some way explain the greater savings achieved there.

Further analysis and explanation of the savings in the prototype refrigerator is not possible owing to the absence of data on such potential causative factors as door opening and room temperatures.

6. Consumer Reaction Analysis

By examining factors that consumers like and dislike, manufacturers can improve product design and make the product more appealing. This information is also useful to discover how to best promote a new product, or to promote existing products in new markets. These were the reasons underlying the development of a consumer opinion portion of the household survey questionnaire. This section summarizes consumer reactions to the 85 prototype units that were placed in the three cities for field testing.

Satisfaction Ratings

Participating households were asked to list their top two likes and dislikes about the prototype. Households were given a list of ten features from which to choose, and an opportunity to add features of their own selection to the list.

When participating households were asked what they liked most about the prototype, 62% of responses listed storage capacity. The new model, at 222 liters, provided 35 percent more space than the average of the refrigerators replaced (the increase ranged from 0% to 122%). Additional factors rated as highly desirable include the prototype's styling and temperature reliability. While few households listed the prototype's beneficial environmental impact as one of the primary desirable features, a significant number of households listed this feature as their second (29 out of a total of 98 second-choice responses) choice, making this the second most highly ranked feature overall. Relatively few households listed the prototype's energy efficiency as a desirable feature, even though over two-thirds of the households reported lower energy consumption after installation of the prototype

Three features were highlighted by households as unsatisfactory. The most disliked feature (39 of 86 responses, or 45%) was noisy operation. Notably, 38 of a total of 65 respondents (58%) listed this as their first selection regarding the prototype's most unsatisfactory feature. The feature listed next most often as unsatisfactory was the lack of an automatic defrost system (23%), followed by unattractive styling (16%). Also notable is that more respondents listed unattractive styling as their first most unattractive feature than listed lack of an automatic defrost system (11 versus 7 respectively). However, none of the households that responded to this question found the new model a poor value for the money. It is also interesting to note that there were significantly more 'likes' than 'dislikes' listed (218 versus 86) in evaluation of the prototype.

Energy Use

Participating households were asked if they noticed a difference in their electricity usage since installation of the prototype. Of those that reported seeing a difference, 68% reported that they used less electricity after installation of the prototype. For those households which made information available on the rated

power consumption of their previous unit, the decrease in average rated refrigerator electricity use for households reporting less energy use was 0.62 kWh/day, in comparison to 0.41 kWh/day for households which reported an increase in energy use. Households which reported a decrease in energy use had average prototype energy consumption of 0.72 kWh/day, as opposed to 0.85 kWh/day (18% higher) for households which reported noticing an increase in energy use. Those households that reported noticing an increase in their energy use had, on average, relatively smaller models of the old refrigerators that consumed less electricity (the average of all old models was 1.14 kWh/day). The savings from the prototype, therefore, were correspondingly less, and may have been compensated for by an increase in other electricity use.

7. Conclusions

The field testing of the prototype refrigerator demonstrated the technical feasibility of manufacturing a CFC-free, energy-efficient refrigerator for household use. The results of the year-long field test showed that the prototype saves energy—from 22% to 35% depending on location. The savings were, however, slightly less than expected. It is unclear if the lower savings were due to the small number of baseline units in the field or if other factors were present for which data are lacking for analysis.

Among the factors found to have a significant impact on energy consumption of the models were the model type (baseline vs. prototype), location (city), family income, and the presence or absence of air conditioning and a kitchen fan. The limited sample size made it difficult to determine which factors, or combination of factors, played a significant role in influencing energy consumption.

Consumers in general liked the prototype refrigerator and indicated that they would recommend it to their friends. The storage capacity of the refrigerator—in many cases larger than the refrigerator it replaced—was considered its most desirable feature, and consumers felt that the refrigerator performed well in maintaining food at the desired temperature. Significantly, environmental protection was an important factor contributing to consumer satisfaction with the refrigerator. A number of users had concerns about the noise level of the new refrigerator, the lack of an automatic defrost feature, and some felt that the styling was not adequate.

About one-third of households felt that energy consumption increased after installation of the prototype. This response is attributed at least in part to the increase in absolute refrigerator size for most consumers, and may also have been influenced by climate, indoor conditions, and other operating factors. It could also reflect that refrigerator savings were swamped by increased electricity use by other appliances or lighting at the same time.

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A Status Report on the Development of HFC Blowing Agents for Rigid Polyurethane Foams

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INTRODUCTION

The field of blowing agents for rigid polyurethane foams has seen a great deal of upheaval in the recent years. Starting with a situation where CFC-11 was the only blowing agent in use, various alternatives have emerged. Among them, HCFC-141b has become the product of choice when high thermal and fire performance are to be achieved. However, HCFCs are to be phased-out eventually, and therefore it is time to consider a new generation of blowing agents that would have no impact on the ozone layer.

This paper provides an update on actions undertaken by Elf Atochem (leading supplier to the rigid polyurethane foam market with FORANE® 141b) to prepare for the future by developing zero ODP (Ozone Depletion Potential) and high performance alternatives.

This will include our latest laboratory results regarding the evaluation of several liquid and gaseous HFCs (HFC-134a, HFC-245fa, HFC-365mfc, HFC-245eb, HFC-245ca and HFC-236ea) as blowing agents in rigid polyurethane foams. The results of the evaluation of HFC-365mfc and HFC-134a by foam producers or raw material suppliers in different applications will also be presented.

CURRENT REGULATIONS ON OZONE DEPLETING SUBSTANCES

The discovery in the 70-80's that some molecules could have a very severe effect on the ozone layer has prompted the international community to enact stringent regulations on their production and/or uses. From its enactment in 1987 and through its subsequent reviews, the well-known Montreal Protocol has been the regulatory arm chosen by the international community for the control of substances that deplete the ozone layer. This international agreement provides a phase-out schedule that will differ depending on types of substances considered and groups ("developed countries" and "article 5 countries") of countries belong to. For the products used as blowing agents in polyurethane foams, the production of CFCs in developed countries was forbidden on 1/1/1996 according to the Montreal Protocol. The "article 5 countries" will have until 2010 to end their production of CFCs. HCFCs have also been included and have an elimination schedule of 2020 (gradual reduction from 2004 to 2020) for the developed countries and 2040 for the article 5 countries (gradual reduction from 2016 to 2040).

Within the frame of this protocol, some countries such as the United States and the European Union have decided to take further steps towards the total phase-out of all ozone depleting substances. The United States has decided, for example, HCFC-141b will have to be phased-out in 2003. Meanwhile, the European Union has phased-out CFCs on 1/1/1995. It has further placed restrictions on the uses of the HCFCs, limiting them to non-emissive applications such as rigid insulating foams. In the European Union, HCFCs will be eliminated in 2014. This latest regulation can even lead to some unexpected results. In the European Union, using HCFCs for flexible or integral skin polyurethane foams is therefore forbidden, but the use of CFCs is not.

Figure 1 summarizes these regulations. It is necessary to keep the whole picture in mind to understand the current developments in the field of blowing agents for rigid polyurethane foams.

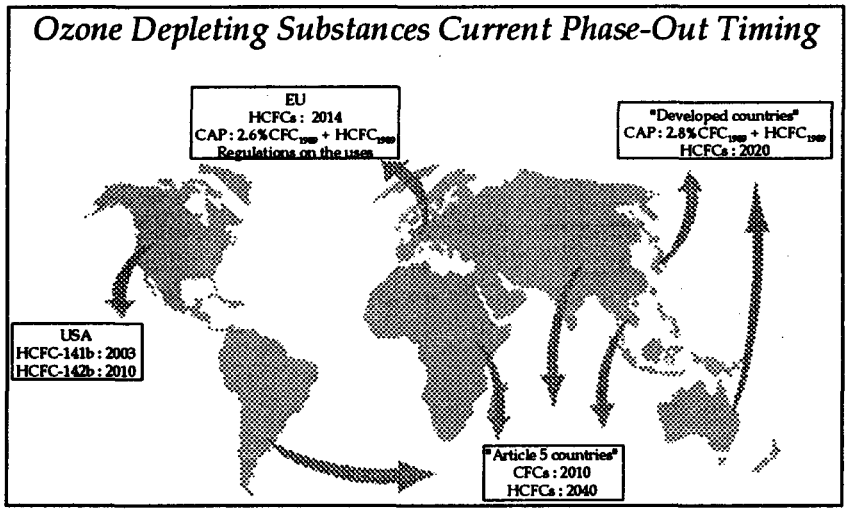

Figure 1. Phase-out schedule for ozone depleting substances

HCFC-141b : A SUCCESSFUL BLOWING AGENT

Since CFCs (CFC-11 in the case of rigid polyurethane foams) have by far the greatest Ozone Depletion Potential (as shown in figure 2), the most effective way to help restore the ozone layer is to stop using them as soon as possible.

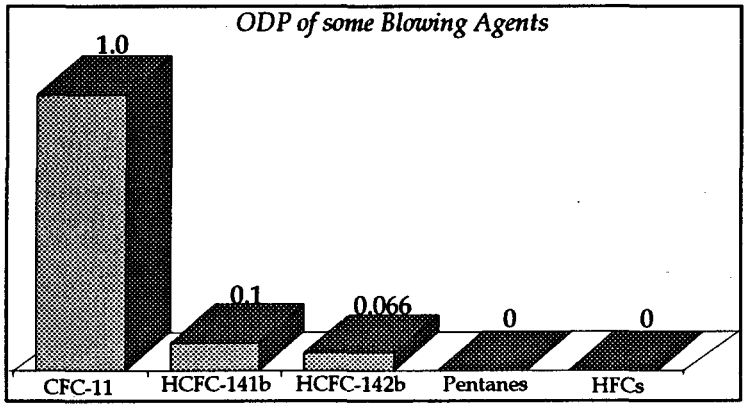

Figure 2. Ozone depletion potential (ODP) of blowing agents

In developed countries, the phase-out of CFC-11 was made possible by the availability of substitutes (HCFC-141b in the US, HCFC-141b and hydrocarbons in the European Union). The phase-out of CFC-11 in foams, along with those ozone depleting substances used in other applications (aerosols, refrigeration, fire extinguishers, ...), , has already proven to be successful. Recent measurements of the atmospheric chlorine loading(1) clearly show that we are on the right track. Indeed, as shown in figure 3, the equivalent effective chlorine content in the northern troposphere (lower layer of the atmosphere) has been decreasing for a few years. Since it takes chemical compounds in the troposphere about 3 years to migrate to the stratosphere (upper layer of the atmosphere - where the ozone layer is), we can expect to observe the same encouraging findings in the stratosphere before the end of the century. Hence, the ozone layer should begin its recovery process very soon despite the fact that the recovery will not be completed until several decades from now.

Therefore, the Montreal Protocol is already a success !

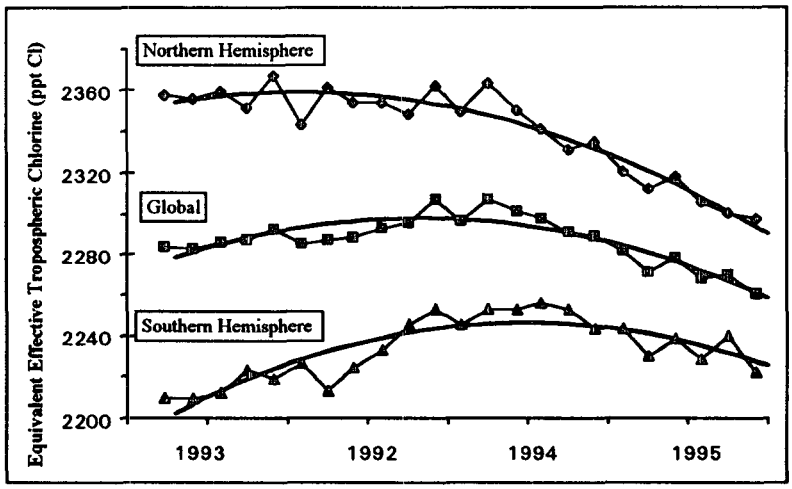

Figure 3. Effective atmospheric chlorine content [1]

Now, the most important issue is to help "article 5" countries to stop using CFCs as quick as possible. HCFCs, especially HCFC-141b, are the easiest and most efficient way to accomplish this goal.

There is a concern that the European Union wants to expedite the total elimination of HCFC-141b. Such decision would have no meaningful effect on the recovery of the ozone layer. Furthermore, it would send a wrong message to the "article 5" countries by encouraging them to continue using CFC-11 until 2010 rather than to switch to a possible threatened blowing agent like HCFC-141b or to hydrocarbons, with large investments to handle the hydrocarbons safely.

In spite of its small effect on the ozone layer, HCFC-141b has proven to be, and still is a necessary step towards the total elimination of CFC-11.

ZERO ODP GASEOUS BLOWING AGENTS

Even if HCFC-141b is still definitely necessary to the rigid polyurethane foam industry, the development of zero ODP substitutes has been ongoing for several years. Among different candidates, HFCs have already appeared to be the most promising candidates. They are efficient blowing agents, safe to handle and have a minimized overall impact on the environment.[2] They have zero Ozone Depletion Potential (ODP), low direct Global Warming Potential, very good energy efficiency and therefore result in a reduced indirect impact on the greenhouse effect (Total Equivalent Warming Impact concept). They also have very low Photochemical Ozone Creation Potential (the HFCs do not participate in the creation of atmospheric pollutant and therefore are not usually classified as Volatile Organic Compounds).

Among the HFCs, it is necessary to distinguish between the gaseous and the liquids ones. Gases are not the preferred options for the expansion of polyurethane foams since they require specific handling procedures, pressure vessels, and may cause some frothing when used. However, since some gaseous HFCs are already available, they can be an appropriate answer for those who want to use a zero ODP, non-flammable blowing agent immediately. HFC-134a, initially developed in refrigeration, is the first obvious choice. Its physical properties are summarized in table 1.

Table 1. Physical properties of blowing agents

Blowing Agent	MW (g/mol)	B.P.(°C)	λgas @25 °C (mW/mK)	Flash Point	Flame lim. (%vol)	ODP	GWP_{100yr}	Toxicity
HCFC-141b	117	32.1	9.7	None	5.8-17.7	0.10	630	Good
134a	102	-26.4	13.5	None	None	0	1300	Good

As reported previously[3], the main drawback of HFC-134a is its limited solubility in most polyols for rigid polyurethane foams. To establish this aspect, its solubility in different polyols has been determined experimentally. The polyols tested are listed in table 2. The solubility measurements are performed as follows:

- a known mass of the polyol, pure or blended, is introduced into an aerosol can,
- a known amount of HFC-134a is then added,
- the can is vigorously stirred for half an hour,
- once the temperature of the can is stabilized at 25°C, the partial pressure of the blowing agent inside the can is measured.

A plot of the blowing agent partial pressure versus the amount of HFC-134a solubilized inside the polyol can be obtained. Figure 4 shows the results gathered for four different polyols with HFC-134a. At a pressure of one bar, the amount of HFC-134a dissolved in polyols can be obtained. This data will indeed correspond roughly to the amount that it will be possible to incorporate in a polyol system and still keep the blend polyol/HFC-134a in a non pressurized container. Except for the aromatic amine based polyether polyol (A3750), the amount of HFC-134a that can be solubilized in the other polyols, for a partial pressure of HFC-134a equal to one bar, is quite constant and is around 0.035 mole/100 g of polyol. This means that around 3.5 parts of HFC-134a can be included in 100 parts of the polyols.

Table 2. Types of polyether polyols

Polyol	Supplier	Polyether type
3750	ARCO	aromatic amine based
3502	ARCO	blend of polyols : sorbitol based and glycerine based
3544	ARCO	sorbitol based
3528	ARCO	sorbitol based

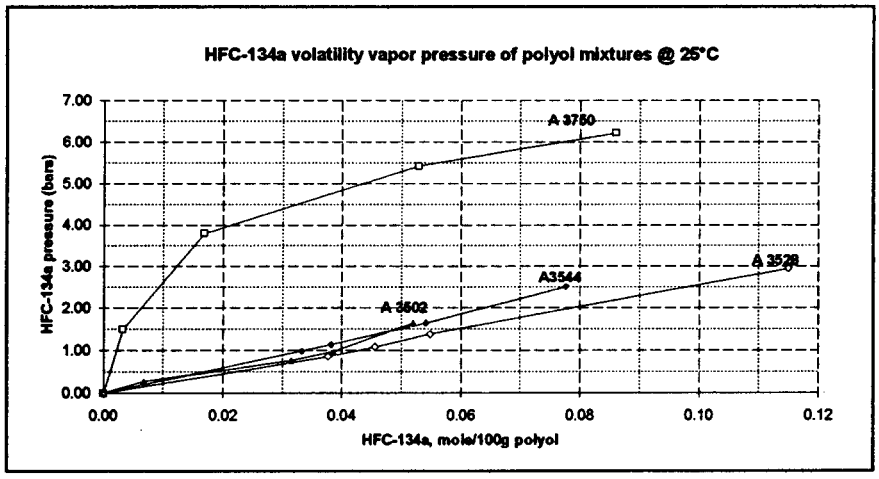

Figure 4. Vapor pressure of 134a in various polyether polyols

HFC-134a industrial scale trials have already been conducted in various locations throughout the European Union. Because of limited solubilities of HFC-134a in polyols, most of systems used so far include only low levels of HFC-134a (2-3 parts of HFC-134a in 100 parts of polyol) and are mostly water co-blown. Table 3 lists typical properties of a foam that can be achieved with a system.

As noted, results are quite satisfactory and can be improved by the use of higher HFC-134a levels, perhaps by the direct injection of HFC-134a at the mixing head.

Table 3. Properties of 134a/H_2O foam

Industrial trial for HFC-134a/H_2O systems in metal faced panels	
Thickness (mm)	70
Core density (g/l)	41.5
Compression set @ 10% (kPa)	140
Open cell content (%)*	2.3
Thermal conductivity @ 24°C (mW/m.K)	
initial	22.4
after ageing (7w @ R.T. + 9w @ 70°C)	23.1
Core cell gas composition : volume fractions Air/CO_2/HFC-134a	
initial	1.6 / 94.7 / 3.7
after ageing (7w @ R.T. + 9w @ 70°C)	23.8 / 68.4 / 7.8
Dimensional stability (% vol. change)	
5d @ 90°C	-4.5
5d @ -18°C	-0.5

* ASTM D 2856 - Procedure B with an initial pressure step of 0.75 psi

ZERO ODP "LIQUID" BLOWING AGENTS - FOAMING TESTS

As we have shown earlier, HFC-134a can be a solution for those who want to use a non-flammable, zero ODP blowing agent immediately. There is, however, still a need for a true "liquid" HFC substitute to HCFC-141b which will be able to replace it in all of its applications. Several candidates have already emerged. A list of those candidates along with their principal physical properties is shown in table 4. Among them, there are three isomers of pentafluoropropane, HFC-365mfc, HFC-236ea and HFE-236 (which is in fact a commercially available molecule used as anaesthetic).

Table 4. Physical properties of blowing agents

	HCFC-141b	HFC-236ea	HFC-365mfc	HFC-245ca	HFC-245eb	HFC-245fa	HFE-236
Formula	CH_3CFCl_2	CF_3CHFCF_2H	$CF_3CH_2CF_2CH_3$	$CFH_2CF_2CF_2H$	CF_3CHFCH_2F	$CF_3CH_2CF_2H$	$CF_3CHFOCF_2H$
MW (g/mol)	117	152	148	134	134	134	168
B.P. (°C)	32.1	6.5	40.0	25.4	22.7	15.3	22.8
d (g/cc)@ 20°C	1.24	1.40	1.25	1.40	1.38	1.32	1.45
λ_{gaz} @ 25°C (mW/m.K)	9.7	11.1*	10.6*	10.8*	11.0*	11.2*	11.6*
Flash point	None	None	-25°C	None	None	None	None
Flame lim. (%vol)	5.8-17.7	None	3.5-9.0	8.3-12.8	9.6-10.7	None	N.A.
ODP	0.10	0	0	0	0	0	0
HGWP	0.14	0.35	0.21	0.15	0.12	0.24	N.A. .
Toxicity	Good	Pending	Pending	Pending	Pending	Pending	Good

*Calculated data

All these molecules were tested as blowing agents in the same conditions. The formulations used are reported in table 5. For comparison purposes, the same polyol/catalyst/surfactant package was used for the six HFCs and HCFC-141b was used as a baseline. Moreover, all the reactants were mixed at 5°C (hand made foams) in order to accommodate HFC-236ea, the blowing agent with the lowest boiling point in this set. An additional group of HCFC-141b foams was also made with all the chemicals kept at 20°C. This allows us to evaluate the influence of initial temperatures. Figures 5, 6 and 7 show the characteristics of the foams obtained with the systems.

Table 5. Foam formulations of different blowing agents

	Temperature of Chemicals (A/B)							
	20°C	5°C						
PU 1832 (BAYER system)	100	100	100	100	100	100	100	100
44v20 (ISO index 105)	163	163	163	163	163	163	163	163
HCFC-141b	21	21						
HFC-245ca			24.4					
HFC-245eb				24.4				
HFC-245fa					24.4			
HFC-236ea						27.7		
HFC-365mfc							27	
HFE 236								30.6
Core density (g/l)	35.8	35.4	36.5	36.5	34.1	33.0	35.9	32.6

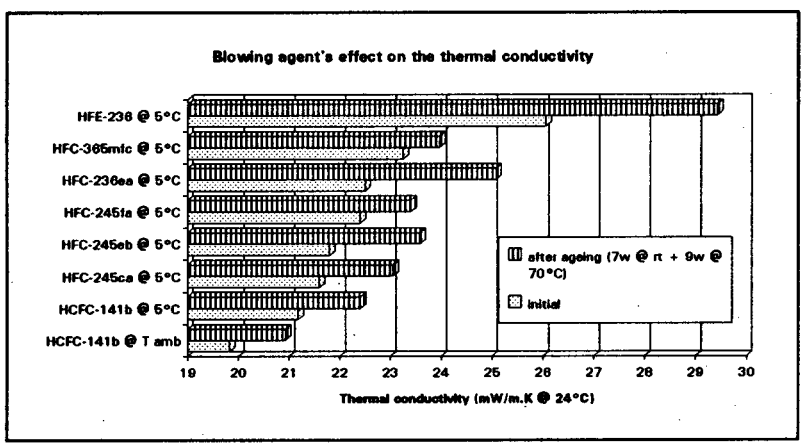

Figure 5. Thermal conductivities of foams with different blowing agents

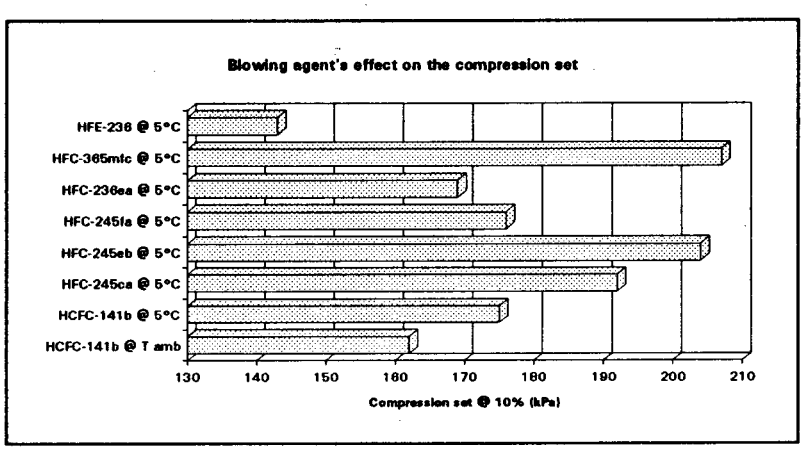

Figure 6. Compressive strength of foams with different blowing agents

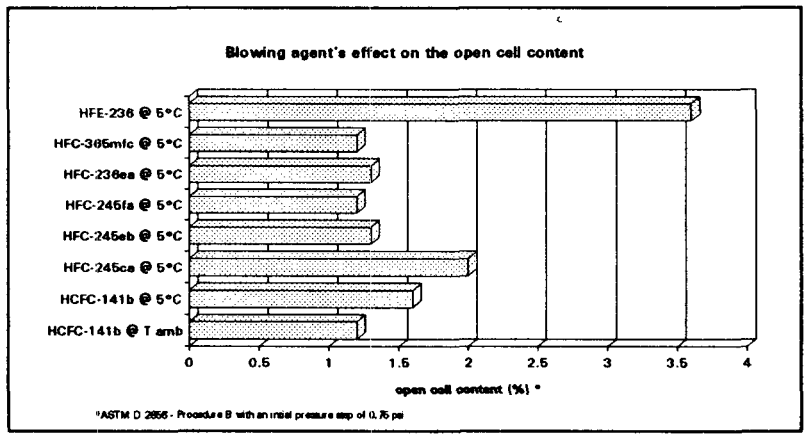

Figure 7. Open cell contents of foams with different blowing agents

From these results, the following trends can be outlined :

- Three pentafluoropropane isomers, namely HFC-245ca, HFC-245eb and HFC-245fa, yield good foam properties in all the areas investigated : thermal conductivity (both initial and aged), compression strength and open cell content.
- For this non-optimized formulation, properties of HFC-365mfc blown foams stand just behind the foams blown with pentafluoropropane isomers. Using a more suitable surfactant (see hereafter) would undoubtedly improve the foam properties.
- It is difficult to control structures of HFC-236ea blown foams because of its relatively low boiling point. There are presence of holes or chimneys in the foams.).
- Even though the characteristics such as boiling point and gaseous phase thermal conductivity of HFE-236 seem to favour this compound as a blowing agent for rigid polyurethane foams , the actual foaming tests reveal that its solubility in the polyurethane matrix is too high to have good foam performance.
- At last, HCFC-141b polyurethane foams blown at 20°C and at 5°C have similar properties.

ZERO ODP "LIQUID" BLOWING AGENTS - COMPARATIVE DIFFUSION STUDY

Long term thermal property of the polyurethane foams blown with these liquid HFCs is another major issue in the substitution of HCFC-141b. One way to deal with this issue is to observe the ageing of foam's thermal conductivity as shown in figure 5. We can also monitor gas phase compositions of polyurethane foams and analyze how fast these blowing agents diffuse out of the polyurethane foams. It was found that the long term thermal efficiency of a closed cell rigid polyurethane foam depends on the diffusion of the blowing agent out of the foam.

As a result, a method has been developed to periodically analyze the content of the gas phase of a cellular polymer. The experimental set-up is relatively easy to implement. Under a helium flow, a syringe needle is pushed inside the foam. Then, the gas phase of broken cells is pulled into the syringe's body. While keeping the needle inside the helium stream, the gas in the syringe is injected in a gas chromatogram and compositions of air, CO_2 and various blowing agents are analyzed. The helium flow is necessary to prevent any outside air from contaminating the original cell gases. This could happen since pressure within the cells might be below atmospheric pressure. With this method, it is thus possible to determine the volume fractions of all the components present in the gas phase of a foam. Therefore, it is possible to follow the evolution of the cell gas compositions with time. To study the comparative diffusion of some of the most likely substitutes relative to HCFC-141b, we prepared two polyurethane foams with a mixture HCFC-141b/HFC-245fa/HFC-365mfc. The initial cell gas contents analyzed according to the above procedure for the two polyurethane samples are shown in table 6. After the initial analysis, one sample was aged at room temperature and the other one was aged at 70°C.

Table 6. Effect of ageing on cell gas compositions

	Initial volume fractions (%)				
	Air	CO_2	HFC-245fa	HCFC-141b	HFC-365mfc
Sample 1 (to be aged @ R.T.)	1.5	38.5	22.4	16.8	20.8
Sample 2 (to be aged @ 70°C)	1.3	40.8	22.1	15.8	20.0

We measured ratios of the volume fractions of HCFC-141b/HFC-245fa and HCFC-141b/HFC-365mfc. Indeed, the volume fraction of HCFC-141b over the volume fraction of HFC-245fa is simply the ratio of the amount of HCFC-141b present in the gaseous phase over the amount of HFC-245fa in this same gaseous phase. The ratios are independent upon the total volume, which would depend on the amount of air or CO_2.

The amount of a physical blowing agent (HCFC-141b, HFC-245fa or HFC-365mfc) in the gaseous phase decreases through several mechanisms: diffusion of the blowing agent out of the foam, dissolution inside the polymer matrix and/or condensation within the cells. The only possibility to observe an increasing amount of blowing agent would have to come from a desorption from the matrix into the gas phase. Under normal circumstances, this is unlikely to happen. For example, if the ratio of the volume fractions of HCFC-141b/HFC-245fa is increasing, it suggests that the amount of HFC-245fa in the gas phase has decreased faster than that of HCFC-141b. On the other hand, if this ratio decreases, it means that the amount of HCFC-141b has decreased faster than that of HFC-245fa. Figure 8 and figure 9 show the evolution of the ratios HCFC-141b/HFC-245fa and HCFC-141b/HFC-365mfc for the polyurethane samples aged at room temperature and 70°C, respectively.

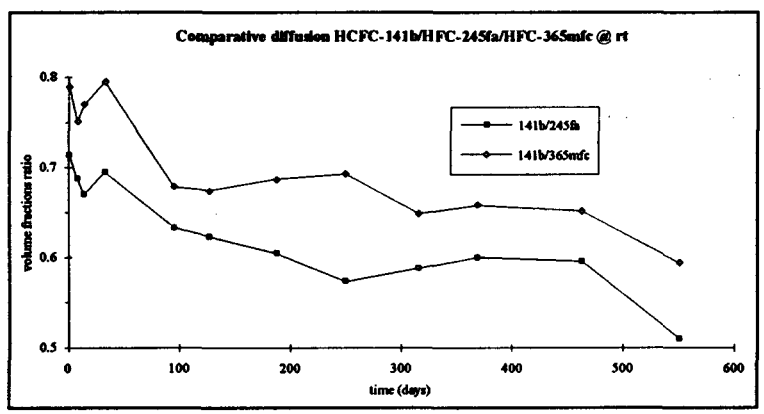

Figure 8. Changes of cell gas compositions of a foam aged at room temperature

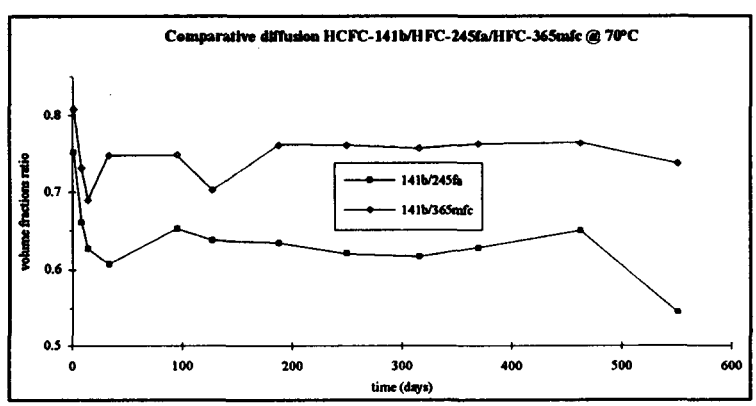

Figure 9. Changes of cell gas compositions of a foam aged at 70 °C

At room temperature, the ratios of the volume fractions of HCFC-141b/HFC-245fa and HCFC-141b/HFC-365mfc decrease with time. This means that HCFC-141b disappears from the foam's gas phase faster than HFC-245fa and HFC-365mfc. Therefore, we can expect a slower ageing (better aged thermal conductivity) from a polyurethane foam blown with either of these two HFCs than with HCFC-141b. As for the evolution at 70°C, the

ratios have a marked decline at the beginning and stay constant afterward. From this comparative diffusion study, we expect that long term thermal ageing of the HFC-245fa and HFC-365mfc blown foams should be at least as good as HCFC-141b blown foam. Our results show that efficient zero ODP substitutes for HCFC-141b do exist. Among them, HFC-245fa and HFC-365mfc appear to be the most promising when not only their performance as blowing agents for rigid polyurethane foams but also their ease of manufacture is considered. Moreover, HFC-365mfc has one more advantage over the other candidates since it can be a HCFC-141b substitute not only as a blowing agent but also as a solvent. This would expand its potential market, and therefore favourably impact its economics.

ZERO ODP "LIQUID" BLOWING AGENTS - HFC-365MFC CUSTOMERS EVALUATIONS

All these facts have prompted Elf Atochem to pursue the evaluation of HFC-365mfc in collaboration with several PUR foam producers or raw material suppliers. As an example, OSi Specialties S.A. has been working on the identification of silicone surfactants especially suitable for HFC-365mfc based systems. Table 7 lists a typical laminated board formulation that was used by OSi Specialties.

Table 7. Typical HFC-365mfc foam formulation

	Surfactants evaluation for HFC-365mfc based systems by OSi Specialties S.A.
Polyol	100
Isocyanate	175
Water	1.8
DMCHA	1.5
Silicone	0.3 to 1.5
HFC-365mfc	31

Table 8 provides some of the results and shows that NIAX® L-6900 and L-6908 seem to give excellent performance with HFC-365mfc systems in terms of both foam flowability and thermal conductivity.

Table 8. HFC-365mfc foam properties

	Surfactant evaluation for HFC-365mfc based systems by OSi Specialties S.A.		
	HFC-365mfc - Flowability* (cm/g)	HFC-365mfc - Initial λ-value (mW/m.K @ 24°C)**	HCFC-141b (reference) - Initial λ-value (mW/m.K @ 24°C)**
NIAX® L-6900	0.95	22.7	22.1
NIAX® L-6908	0.93	23.0	21.7
NIAX® SR-321	0.72	23.1	/

*0.3 part of silicone
**1.5 part of silicone - Moulded foam : 34g/l - Free rise density : 25.0g/l

Finally, HFC-365mfc has also been evaluated by Industrial Urethanes (system supplier - South Africa) using the formulation described in table 9. The results are presented in table 10.

These results are again very encouraging and clearly demonstrate the potential of HFC-365mfc as a blowing agent for rigid polyurethane foams.

Table 9. HFC-365mfc foam formulation by Industrial Urethanes

	HFC-365mfc evaluation by Industrial Urethanes (system supplier - South Africa)
Polyol blend	79.8
Isocyanate (index 110)	128
Water	1.8
HFC-365mfc	18.4

Table 10. HFC-365mfc foam properties by Industrial Urethanes

HFC-365mfc evaluation by Industrial Urethanes (system supplier - South Africa)	
Cream time (hand mix)	15 seconds
String time	67 seconds
Tack free time	103 seconds
Free rise density	25.6 kg/m^3
Initial K-value @ 10°C	22.1 mW/m.K
Compression strength 10% Samples from Brett Mould (foam core density 31.8kg/m^3)	247.4 kPa (parallel to rise) 106.0 kPa (perpendicular to rise)

CONCLUSION

Several zero ODP HFCs, ranging from gaseous to liquid blowing agents, have been evaluated. The results show that there are promising candidates that can be used to replace HCFC-141b. Many factors (environmental impact, toxicity, flammability and foam performance) must be considered to qualify a candidate as an acceptable blowing agent. Meanwhile, other factors such as availability of feedstock, ease of manufacture, cost and market size must also be considered for a candidate to be selected as a commercial product. The objective for Elf Atochem is to determine the best option. This is followed by long term toxicological studies, pilot and plant construction and reformulation.

ACKNOWLEDGEMENTS

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BIOGRAPHICAL NOTES

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New Generation EPS Foam
Economical and Ecological Insulation Alternative

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ABSTRACT

Insulating EPS foams offer ecological and economical performance not attained by any other rigid foam material. However, due to radiative heat losses at low densities, they incur the penalty of either increased thickness or density: optimum thermal conductivity requires a bulk density above ca. 30 g/l, while at low densities of 10 g/l and below, their thermal conductivity is about twice that of competitive (PUR) foams.

During recent years, Schwenk and BASF have successfully embarked on a program to develop a commercial production process for a superinsulating EPS that has low thermal conductivity in the low density range. A unique inner microscopic structure which blocks radiative heat exchange allows a conductivity λ_{10} of 30 mW/m*K to be achieved at 14 g/l.

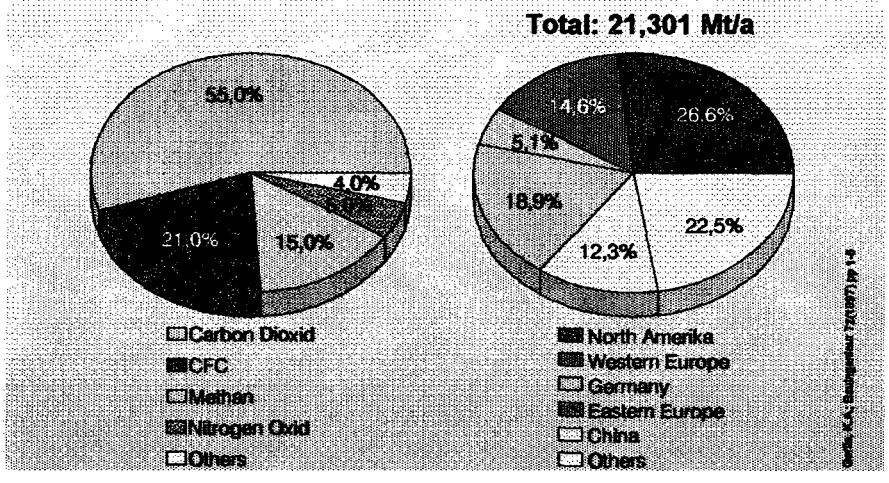
This superinsulating EPS foam has been developed to a precommercial stage. Large scale processing of the material has been successful and is being further developed.

In the future, this new foam material may achieve a significant contribution toward further improving the energy balance of buildings and economical balances in domestic appliances. The excellent quality of the super insulating EPS gives a remarkable 50% improvement over conventional foamed insulation systems in terms of raw material consumption and costs.

INTRODUCTION

The emissions of various gases to the atmosphere and CO_2 emissions from the world's major regions and countries are shown in Figure 1. Owing to its greenhouse properties, CO_2 has become a serious risk to our earth. With a 55% share, it is the major contributor to this effect. CO_2 emissions should therefore be reduced with all available means.

Fig. 1: left: Contribution of Gases to the Greenhous Effect
right: Worldwide Emission of Carbon Dioxide, 1995

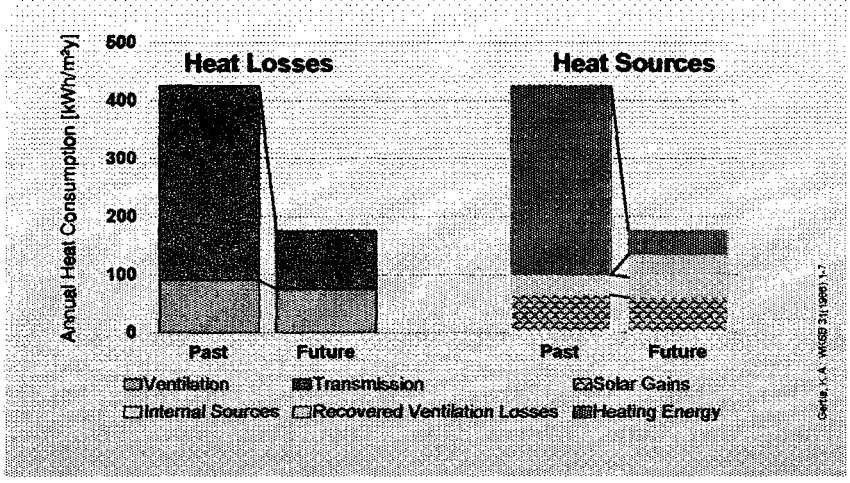


Western Europe, Eastern Europe, North America and China are the major producers of CO_2 in the world and must in future drastically reduce their emissions

- because the world mean outside temperature has been increasing significantly since the last century as a consequence of the greenhouse effect /1/ and
- because threshold and developing countries will contribute to a further major increase in CO_2 emissions in the future owing to their demand for an increased standard of living.

Optimum thermal insulation of buildings and domestic appliances has been shown *to be one of the most successful strategies for avoiding unnecessary emissions of* CO_2 during energy production for heating buildings and water /2/. Improved thermal insulation saves energy and reduces the quantity of CO_2 emitted to the atmosphere.

Fig. 2: Energy Balance of Single-Family Homes



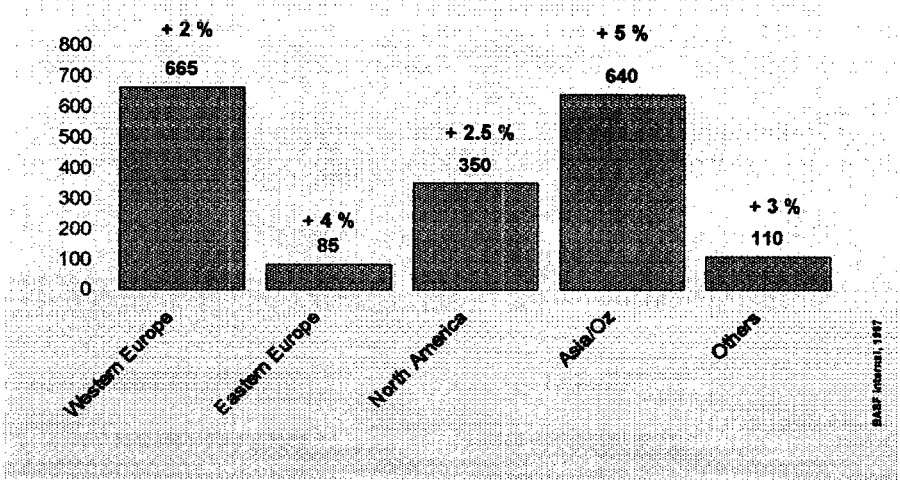
The great potential for rigorous energy savings is shown in Figure 2, in which the energy losses from buildings is compared with energy sources. It will be possible in the future to reduce the heating energy for a house built to the latest standards to about one tenth (low energy houses: 30-40 kWh/m^{2}y, passive solar heated houses: < 15 kWh/m^{2}y) of the requirement of former years /3,4/. If ventilation losses are assumed to be more or less constant, the main contribution to the drastically reduced heating energy requirement is good thermal insulation of the outer walls with EPS insulation boards, which are available up to 27 cm thick. This requires thermal insulation materials which

- have an extremely good cost/benefit ratio, offering considerable attraction for investment in thermal insulation upgrades,
- achieve the maximum potential for saving energy and raw materials through leading edge performance, and
- have a zero ozone depletion potential.

MARKET REQUIREMENTS

Of all the alternative thermal insulation systems, EPS foams represent the best option in ecological and economic terms. They have never been produced with CFCs or HCFCs and offer an unrivaled overall property profile. 45 years after the invention of EPS the success of EPS foams in insulation markets is still being sustained today (Figure 3).

Fig. 3: Regional EPS Market Structure
Expected Growth per Year



EPS has played a full part in the gratifying growth of thermal insulation volumes as a consequence of increased environmental awareness (for example, >75% growth in Germany between 1990 and 1996, 7% in Western Europe in 1996). The current

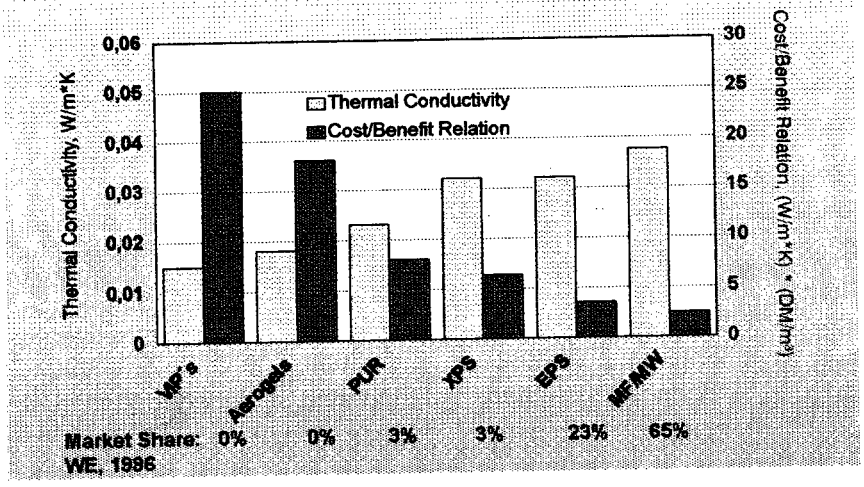
market volume is greater than 10 million m^3 in Germany and more than 28 million m^3 in Western Europe.

Besides the material's versatility and adaptability to a wide range of requirements, a particular reason for this success with almost 2 million metric tons EPS per year worldwide is its excellent performance.

For thermal insulation materials where assessment of performance is relatively clear, reference /5/ presents a method for an approximate evaluation based on the cost/benefit ratio.

The most economical competitor, Mineral Fiber MF/MW, in spite of unsatisfactory thermal insulation (light bar), dominates the European market with a share of approximately 2/3 (Figure 4). All other positions correspond to the cost ranking, shown by the dark bars: EPS 23%, XPS 3%, PUR 3%, others 5%. This strong "market pull" has not yet been successfully overcome, in particular by "alternative" insulation materials, in spite of widely discussed society demand /6/.

Fig.4: Performance Profile and Cost/Benefit Relation of Thermal Insulation Materials



Expensive thermal insulation materials can easily be substituted where only thermal insulation is required achieve their market share by offering a combination of benefits "insulation + X". EPS (or XPS) is a good example of this thanks to its toxicological acceptability and superior property profile compared to the market leader MW in a range of applications. PUR is successfully defending its leading position in the domestic appliance industry since low λ values have priority over lower prices at limited insulation thicknesses. The development of the extremely "uneconomical" VIPs (vacuum insulated panels /7/) has also been helped by this.

The converse argument also applies: aerogels have so far been without commercial success in competitive markets, in spite of their highly attractive technical performance, because it has not been possible to provide an additional benefit which would justify the price premium that arises from the complex production technology /5/.

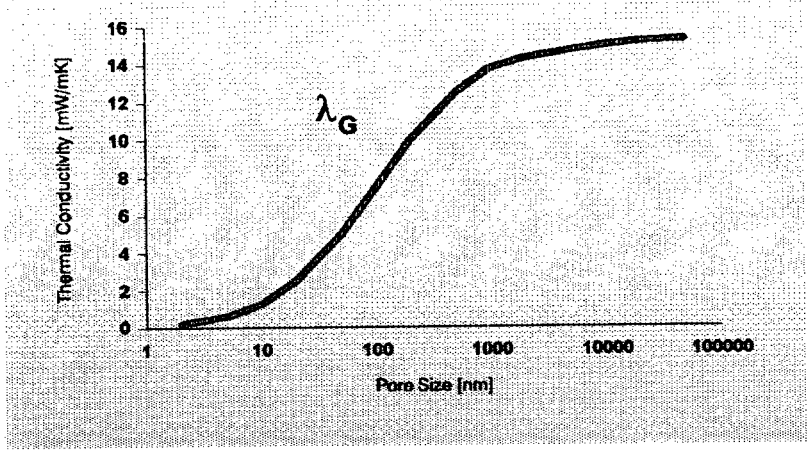
DEVELOPMENTAL APPROACH

Gaseous heat transfer (Convection)

Specially designed cell structures containing air or other gases can reduce heat losses of thermal insulation foams caused by gas conduction. Potential cell gases (for example blowing agents) differ considerably in their thermal conductivity, which has ultimately resulted in significant use of ozone-depleting CFCs.

Figure 5 shows for example the theoretical correlation between cell size and the thermal conductivity of CO_2-foamed PUR systems. The thermal conductivity of CO_2 gas, λ_G, drops to a greater extent as the cell size approaches the mean free path length of the gas molecules (about 50 nm).

Fig. 5: Gaseous Heat Losses (CO2) for PUR as a Function of Pore Size

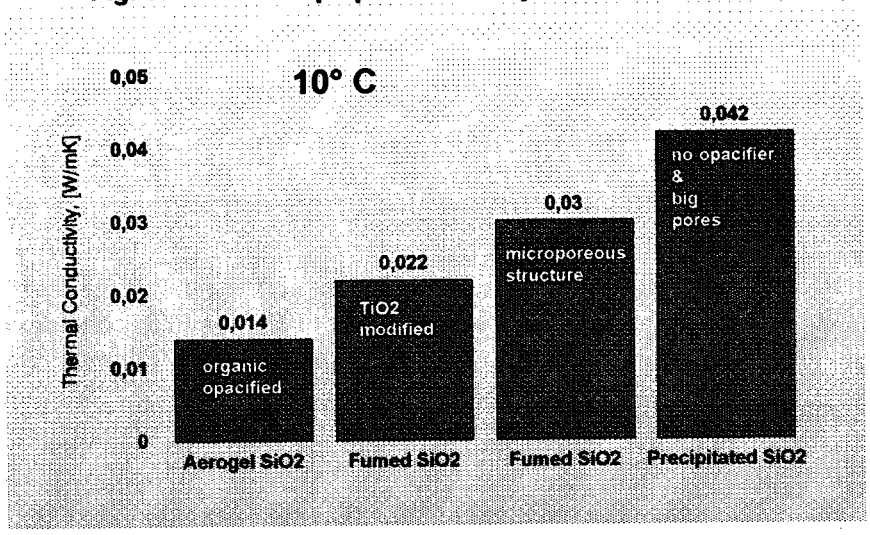


Low density mineral fiber/mineral wool with its open, fibrous structure with a thermal conductivity of 40 mW/m*K therefore provides only about 75% of the thermal protection of a closed-cell EPS (30 mW/m*K). Blowing agents of low thermal conductivity and a better-optimized cell structure and size virtually halve the value in PUR systems (< 23 mW/m*K). Better performance can only be achieved by means of the special nanostructure of aerogels (14 - 18 mW/m*K).

Radiative heat transfer

Energy absorbers and dispersers, such as carbon black, TiO_2, etc., are a second known way of reducing heat losses of insulation materials by minimizing the radiative components λ_R. This effect is shown in Figure 6 by a comparison of various silicas.

Fig. 6: Effect of Opaqueness for Synthetic SiO2



Conductive heat transfer

Solid conduction λ_S, the third component of heat transfer, is a physical constant. Choice of materials also contributes to the development of good thermal insulation materials. The success of organic thermal insulation materials in the past is attributable not least to the fact that their performance in this respect is very positive: PS 0.14 W/m*K, PUR 0.15 W/m*K, MF 0.22 W/m*K, compared, for example, with SiO_2 at 1.34 W/m*K /8/. Correspondingly low thermal conductivities are shown by EPS insulation materials.

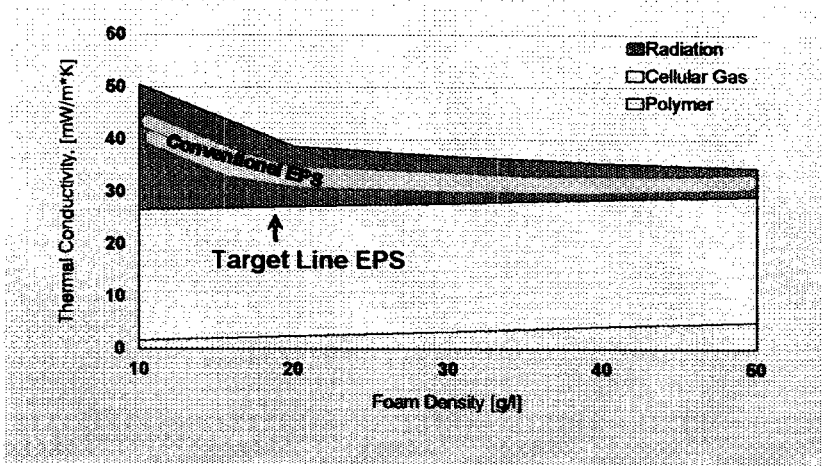
The summation of the three individual components of heat transfer, which can be determined very precisely by physical methods, gives the thermal conductivity

$$\lambda = \lambda_G + \lambda_C + \lambda_S.$$

Figure 7 shows the results of analysis of the heat transfer components in EPS. It is clearly evident that the radiative component is particularly important at low densities.

Regarding the generally observed mutual effects of cell design and optimization of radiative and conductive losses, we refer to the literature /9/.

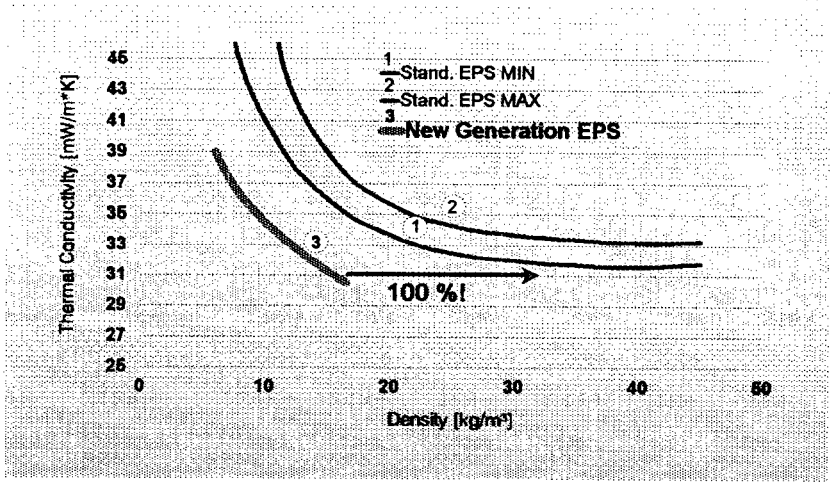
Fig. 7: Foam Density of EPS vs Optimum Thermal Conductivity and it´s Components



These results, in particular the effect of absorption and scattering of infrared radiation in silicas, have now allowed the pilot-scale production of a polymer whose suitability for thermal insulation is far superior to that of conventional EPS (Figure 8). In the low-density range of 15 g/l or less, which is of interest in construction and for economic reasons, the thermal conductivity of around 27 mW/m*K is close to the theoretical minimum which can be achieved with a radiative loss of 0. At lower densities of < 10 g/l, this theoretical value is increasingly difficult to attain. The very thin cell membranes are increasingly difficult to "seal" against transmission of the infrared radiative component.

Regarding the extent of the improvement over conventional EPS, while the attainment of a λ value of 31 mW/m*K in the past required at least 30 kg of raw material per cubic meter, this insulation performance can now be achieved by the new generation of EPS material using about half the amount of raw material.

Fig. 8: Thermal Insulation of Conventionel EPS and New Generation EPS



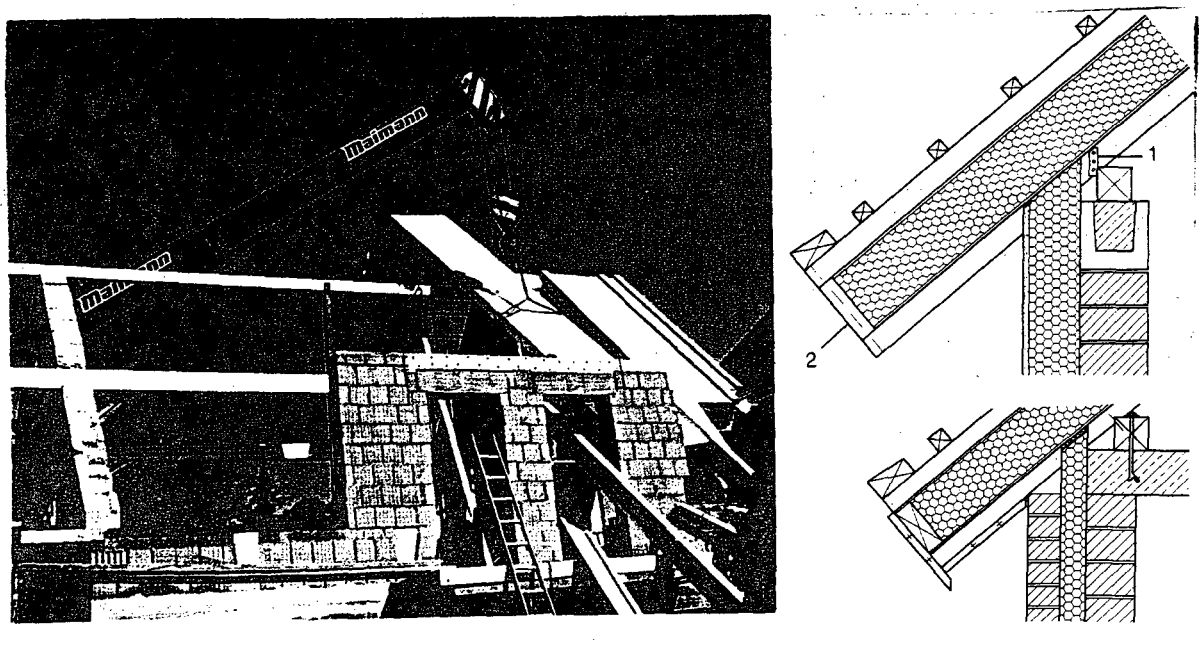
APPLICATIONS AND BENEFITS

EPS boards for outer wall insulation, which are cut from slabs in thicknesses of up to 27 cm (low energy houses), are difficult to produce at greater thicknesses avoiding warping due to internal stresses and dimensional tolerances. In addition, the shear stresses generated in external wall thermal insulation systems between the outer plaster and the supporting wall construction are also increasingly difficult to bear with increasing thickness of the EPS insulation layer. Reduced thicknesses of EPS insulation material with the same insulation capacity significantly helps to solve this problem and reduce processing costs.

Other interesting applications will be in cavity walls and multilayer plasterboard for internal insulation. A particularly interesting application will be in composite elements for sloped roofs (Figure 9), where the thickness of the EPS insulating boards frequently (over-)determines the dimensions of the construction. If the elements required for insulation could be made thinner in order to achieve optimum insulation, this would have a considerable impact on construction methods and costs as a whole.

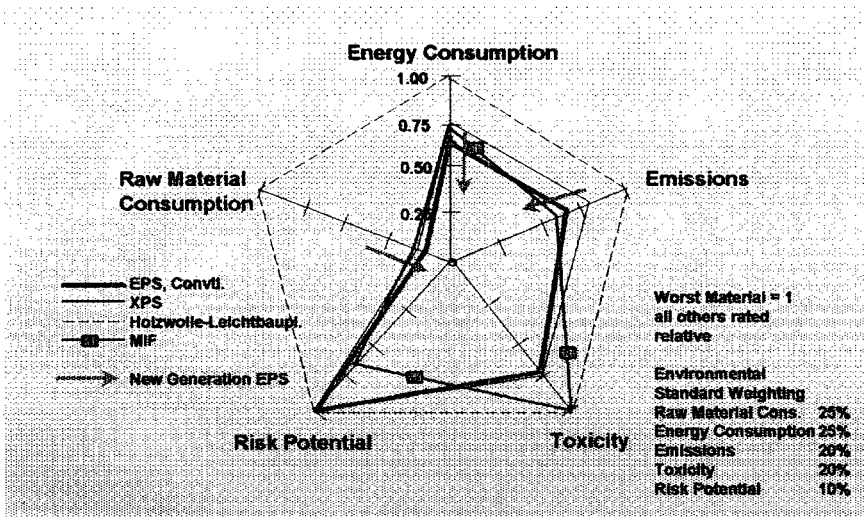
Finally, in the renovation of old buildings, every centimeter of insulation material that can be saved in sound transmission insulation and in the underfloor heating insulating boards for the same insulation value allows a centimeter more room height.

Fig. 9: Prefabricated Structural Composite Elements for Roof Construction /10/



In domestic appliance segments that are important for insulation materials, namely refrigeration and hot water tanks, the minimal insulation thickness requirements have meant that the main material used has been PUR, although it has a worse cost/benefit ratio and in no way fully satisfys today's recyclability requirements. It will be interesting to see how the new material, which offers significantly improved economic potential, will succeed in winning market share from other attractive materials.

Fig. 8: Ecological Finger Print of Thermal Insulation Systems /9/



In an ecoefficiency analysis (Figure 8), EPS is compared with XPS and lightweight wood fiber construction boards (outer layer magnesite + wood fiber, core EPS). In order to achieve the same insulation effect, the thickness of the PS materials was assumed to be 4 cm and that of the mineral-bound board 5 cm. The comparison was carried out over the life of the building. The environmental impact can be described using 5 criteria: material consumption, energy consumption, emissions, toxicity and risk potential /9/.

In all criteria, even conventional EPS is superior to the competing materials. The new generation EPS will provide further improvements, in particular in raw material consumption and emissions (green arrows). For the foreseeable future this situation is not expected to change.

SUMMARY

The special ecological benefits of the superinsulating EPS insulation material innovation described here make possible the

- saving of valuable raw materials of up to 50% and the corresponding,
- saving of energy and avoidance of emissions during production, and the
- development of new areas of application (domestic appliance industry, inter alia) which were in the past the domain of ecologically less acceptable insulating materials.

Economic benefits come from the considerable simplification of the design of insulation systems.

The development of a process for production of the new material on a commercial scale is being pursued with vigor.

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HCFCs AND HFCs BLOWING AGENTS FOR XPS INSULATING BOARDS

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ABSTRACT

The Montreal Protocol and its subsequent reviews have presented a great challenge for the XPS (extruded expanded polystyrene) foam industry. Indeed, CFC-12 has long been the blowing agent of choice in that application due to its unique properties such as non-flammability, non-toxicity, low thermal conductivity and good processability.

In developed countries, the rapid phase-out of CFC-12 was made possible thanks to the availability of HCFCs: HCFC-142b, pure or in blends with HCFC-22 or ethyl chloride, has now become the reference blowing agent for XPS insulating boards world-wide owing to its superior properties.

This paper will discuss the current situation by providing some information about properties commonly found in laminated boards. A theoretical model will be used to simulate their long term behaviour, especially thermal insulation.

Using this theoretical model and available data, it enables us to have an insight of the foam performance that can be achieved by zero ODP (Ozone Depletion Potential) substitutes such as HFCs and carbon dioxide. HFC-134a appears to be the most promising one, particularly when the thermal insulation is needed.

BLOWING AGENTS FOR XPS INSULATING BOARDS: CURRENT SITUATION

XPS (extruded expanded polystyrene) foams represent a very versatile class of materials. They are used in various areas such as packaging and construction industries. As a construction material, XPS insulating boards are especially suited when good mechanical properties, moisture resistance and thermal efficiency are required. Thanks to these properties, XPS insulating boards have almost the same market share as polyurethane foams used as construction insulation materials in France and Germany [1].

Certainly, blowing agents used for the production of XPS boards will have a large influence on the boards' final properties. This is because they will be retained within the foam's closed cells. This is why CFC-12 has long been the blowing agent of choice, due to a combination of unique properties such as non-flammability, non-toxicity, low thermal conductivity and good processability. However, the concern that CFCs might have contributed to the depletion of the ozone layer has prompted the international community to move towards their elimination through the implementation of the Montreal Protocol that will be detailed in the next chapter.

The rapid phase-out of CFC-12 in developed countries was made possible thanks to the availability of HCFCs: HCFC-142b, pure or blends with HCFC-22 and ethyl chloride, has now become the reference blowing agent for XPS insulating boards owing to its superior properties. Table 1 lists characteristics of these HCFCs, CFC-12 and other potential substitutes.

In the United States, HCFC-142b has been chosen for production of XPS boards. A small amount of a co-blowing agent such as ethyl chloride is also used. In Europe, most manufactures have chosen to use a blend of HCFC-142b and HCFC-22. This blend is non-flammable and therefore the investments that would have resulted from the use of a flammable product like pure HCFC-142b can be avoided. In most instances, a non-flammable blend of HCFC-142b/HCFC-22, 60/40 by weight, was chosen. In some cases, pure HCFC-142b, together with a small amount of a low molecular weight alcohol such as ethanol, can also be found in the European market. A recent development has been the applications of zero ODP blowing agents such as liquid carbon dioxide or HFCs

(HFC-134a and HFC-152a) in Germany and northern Europe . They were developed at the initiative of some XPS boards producers to respond to stringent local regulations such as the phase-out of HCFC-142b in Sweden as of January 1st, 1997. The performance of boards made by these zero ODP alternatives will be discussed later.

Table 1. Physical properties of blowing agents

	CFC-12	HCFC-142b	HCFC-22	HFC-134a	HFC-152a	CO_2
Formula	CF_2Cl_2	CH_3CF_2Cl	CHF_2Cl	CF_3CFH_2	CH_3CF_2H	CO_2
MW (g/mol)	120.9	100.5	86.5	102.0	66.0	44.0
B.P. (°C)	-29.8	-9.6	-40.8	-26.4	-24.7	/
P_{sat} @ 25°C (bars)	6.5	3.4	10.4	6.6	6.1	64.3
λ_{gas} @ 25°C (mW/m.K)	9.6	11.5	11.0	13.6	13.4	16.6
Fl. Lim. (%vol)	None	9.0-14.8	None	None	3.7-18.0	None
ODP	0.9	0.066	0.05	0	0	0
$GWP_{100\,yr}$	8500	2000	1700	1300	140	1

CURRENT REGULATIONS ON OZONE DEPLETING SUBSTANCES

The discovery in the 70-80's that some molecules could have a very severe effect on the ozone layer has prompted the international community to enact stringent regulations on their production and/or uses. From its enactment in 1987 and through its subsequent reviews, the now well-known Montreal Protocol has been the regulatory arm chosen by the international community for the control of substances that deplete the ozone layer. This international agreement provides a phase-out schedule that will differ depending on the type of substance considered and the group the country belongs to ("developed countries" and "article 5 countries"). According to the Montreal Protocol, the production of CFCs in the developed countries was forbidden on 1/1/1996. The "article 5 countries" will have until 2010 to end their production. HCFCs have also been included and have an elimination schedule of 2020 (gradual reduction from 2004 to 2020) for the developed countries and 2040 for the article 5 countries (gradual reduction from 2016 to 2040).

Within the frame of this protocol, some countries such as the United States and the European Union, have decided to take further steps towards the total phase-out of all ozone depleting substances. The United States has decided, for example, HCFC-141b will have to be phased-out in 2003 and HCFC-142b in 2010. Meanwhile, the European Union has phased-out CFCs on 1/1/1995. It has further placed restrictions on the uses of the HCFCs, limiting them to non-emissive applications, such as rigid insulating foams. In the European Union, HCFCs will be eliminated in 2014. Figure 1 summarizes these regulations.

The phase-out of CFCs in foams (CFC-12 for XPS boards, CFC-11 for polyurethane foams), along with those made by the other application sectors (aerosols, refrigeration, fire extinguishers, ...), which were using ozone depleting substances, has already proven to be successful. This is demonstrated by recent measurements of the atmospheric chlorine loading [2]. As shown in figure 2, the equivalent effective chlorine content in the northern troposphere (lower layer of the atmosphere) has been decreasing for a few years. Since chemical compounds in the troposphere need about 3 years to migrate to the stratosphere (upper layer of the atmosphere - where the ozone layer is), we can expect to observe the same encouraging findings in the stratosphere before the end of the century ; hence, the ozone layer should begin its recovery process very soon despite the fact that the recovery will not be completed until several decades from now.

Therefore, the Montreal Protocol is already a success !

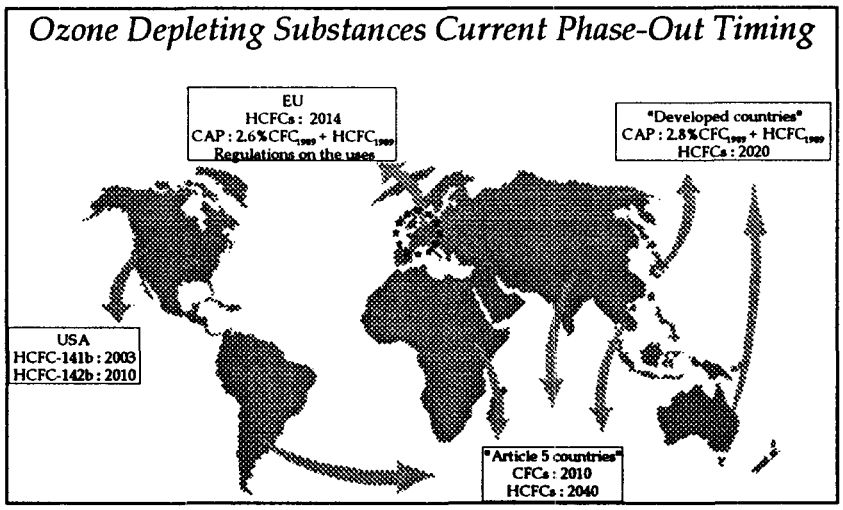


Figure 1. Phase-out schedule for ozone depleting substances

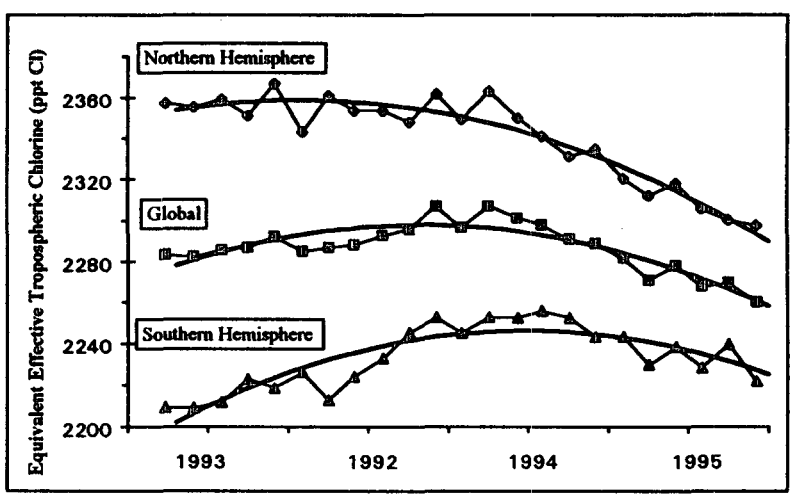


Figure 2. Effective atmospheric chlorine content [2]

HCFCs AS BLOWING AGENTS FOR XPS INSULATING BOARDS

The thermal conductivities of the XPS boards depend on selections of the blowing agents. Indeed, heat transfer through the gaseous phase of the XPS board accounts for roughly 50% of the total heat transfer through the foam. Other contributions result from the heat transfer through the solid polystyrene matrix and also from the radiative heat transfer. Coming back to the main contribution, the heat transfer through the sample is determined by the thermal conductivities of the gaseous phases. Figure 3 lists the gaseous phase thermal conductivities of the major blowing agents for XPS boards.

One should keep in mind that the gas phase composition is going to evolve as time elapses. Air will diffuse into the foams and the blowing agents inside the cells will diffuse out of the foams until the gas phase in the cells reaches an equilibrium with their surroundings (one atmosphere of air and no more blowing agents within the foam cells). Since air has a greater thermal conductivity, this process is going to result in an overall increase of the board's thermal conductivity ; this phenomenon is often referred as ageing.

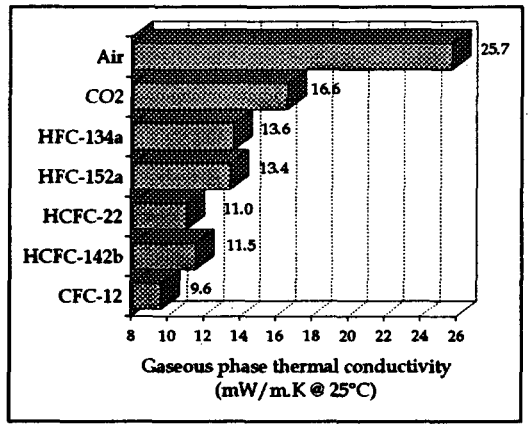


Figure 3. Thermal conductivity of blowing agents

One of the he parameters which govern the foam's ageing rate is the diffusion of the blowing agent out of the board. In order to assess the long term thermal efficiency of an XPS board, it's very important to have an accurate estimation of the parameter. Two methods can be employed to determine the diffusion of a blowing agent out of an XPS foam. The first one uses an actual piece of foam and measures the effective diffusion coefficient of the blowing agent. For example, One can analyze the amount left inside the foam at different times; In that case, the adjective "effective" relates to the fact that the diffusion coefficient is measured for a given piece of foam, with all of its structural parameters, and not for a bulk polystyrene. The other method is to use a bulk polystyrene and determine the permeability of a molecule through this polymer by using, for example, a permeation cell.

It is difficult to compare the numerical value of its effective diffusion coefficient of a blowing agent through an XPS board with its permeability in bulk polystyrene. It is nevertheless possible to compare the ratio of two effective diffusion coefficients to the ratio of the corresponding permeabilities in polystyrene. For two blowing agents (i & j), the following expression has been established [3]:

$$\frac{D_{eff,i}}{D_{eff,j}} = \frac{P_i}{P_j} \times f(\text{foam's void fraction, ...})$$

Where D_{eff} represents the effective diffusion coefficient of the blowing agent through the XPS foam and P represents its permeability in the bulk polystyrene.

For a typical XPS foam, with a very high void fraction, the second right hand term always remains close to one. This means that the ratio of the effective diffusion coefficients of two blowing agents through an XPS board is almost the same as the ratio of their permeabilities in the bulk polystyrene.

Table 2 shows some data available in the literature regarding the permeability of blowing agents in polystyrene and/or their effective diffusion coefficients through XPS boards. For better comparisons, the ratios of the permeabilities and the effective diffusion coefficients relative to HCFC-142b are calculated. It is noted that the values presented in table 2 differ from one set of data to another (the permeability depends on bulk properties of the polystyrene and the effective diffusion coefficient depends on the foam's structure).

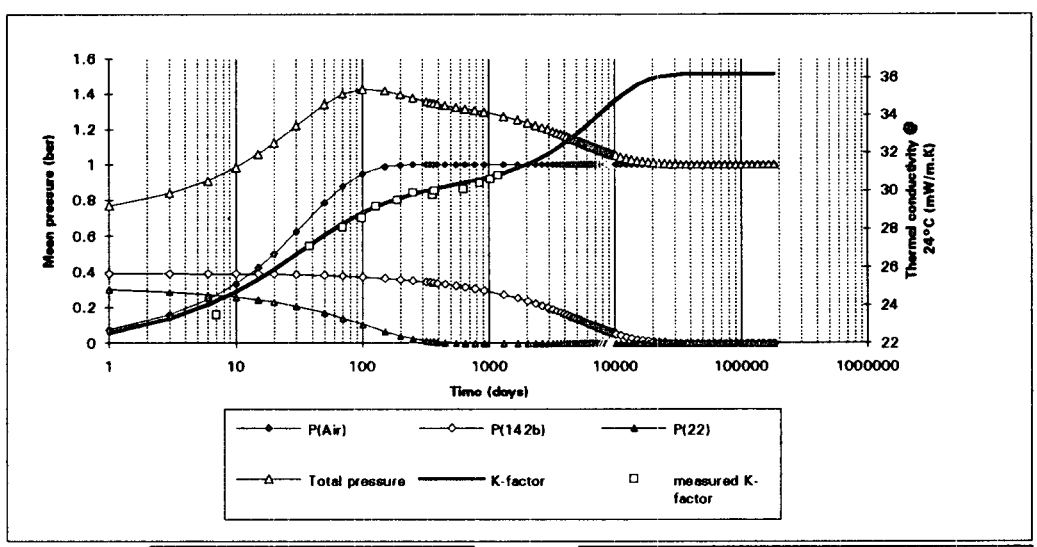
The results shown in Table 2 indicate that HCFC-142b, like CFC-12, can be considered as a permanent blowing agent in the sense that it will stay within the foam cells for a very long period of time (see hereafter) ; HCFC-22, on the other hand, will leave the foam cells faster than that of HCFC-142b, and CO_2 will diffuse out of the cells at a even higher rate.

Thanks to the knowledge of the effective diffusion coefficients of the blowing agents through XPS boards, it is possible to predict the long term thermal conductivity of the boards. Figure 4 shows k-factors of a 30mm thick XPS board (blown with a blend HCFC-142b/HCFC-22 60/40 by weight or 56/44 by volume) at various ageing times. The results are compared with a theoretical simulation which was performed using a mathematical model similar to the one described by Glicksman[8]. The thickness and density of the XPS board were measured experimentally. Other parameters (cell diameter, volume fraction of the polystyrene in the struts - the polystyrene being shared between the struts and the cells' windows -, effective diffusion coefficients of air and the blowing agents) were so determined, within reasonable limits, to have a good agreement between the experimental and theoretical k-factors. It is noteworthy to mention that the values obtained for the effective diffusion coefficients of

HCFC-142b and HCFC-22 are in good agreement with the ones given in table 2.

Table 2. Permeability and effective diffusion coefficient of blowing agents

	Permeability in PS according to [4]	Permeability in PS according to [5]	Effective diffusion coefficient through XPS foam according to [6]	Effective diffusion coefficient through XPS foam according to [7]
	$cm^3_{STP}\ cm/(cm^2\ scmHg)$		m^2/s	
	(with reference to HCFC-142b)			
HCFC-142b	$6.31\ 10^{-13}$ *(1)*	$4.2\ 10^{-14}$ *(1)*	$2.6\ 10^{-13}$ *(1)*	$3.1\ 10^{-13}$ *(1)*
CFC-12	$2.64\ 10^{-13}$ *(0.4)*	$1.1\ 10^{-13}$ *(2.6)*	$2.3\ 10^{-13}$ *(0.9)*	
HCFC-22	$1.67\ 10^{-11}$ *(26)*	$1.1\ 10^{-11}$ *(271)*	$1.8\ 10^{-11}$ *(69)*	$3.1\ 10^{-11}$ *(100)*
HFC-134a	$5.03\ 10^{-13}$ *(0.8)*	$2.1\ 10^{-13}$ *(5)*	$2.9\ 10^{-12}$ *(11)*	
HFC-152a		$5.0\ 10^{-12}$ *(120)*	$1.6\ 10^{-10}$ *(615)*	
C_2H_5Cl		$5.0\ 10^{-11}$ *(1200)*		
CH_3Cl		$5.9\ 10^{-10}$ *(14000)*		
Air		$6.6\ 10^{-11}$ *(1571)*		
CO_2			$1\ 10^{-10}$ *(384)*	



XPS foam	Air	HCFC-142b	HCFC-22
Pressure	0.01	0.39	0.31
Diff. Coeff. (m²/s)	3.00E-11	2.00E-13	1.00E-11

thickness (mm)	density (g/l)	diameter (microns)	Vstrut (%)
30	30.3	250	13

Figure 4. Aging of XPS board

Using the same set of parameters, figure 5 shows effects of the initial blowing agents (pure HCFC-142b versus HCFC-142b/HCFC-22 60/40 by weight) and of the foam thickness (30mm versus 80mm).

Table 3 summarizes the mean thermal conductivities over several periods of time (from one to one hundred years) based on the simulation. When CO_2 is used as the blowing agent , the thickness has no effect on the board's thermal conductivity since CO_2 is replaced by air in a matter of days or weeks. The range of thermal conductivities reported in the table for CO_2 blown boards correspond to different commercially available XPS foams : between 34 and 37 mW/m.K @ 24°C, both are constant through times. The difference is primarily caused by the foam's structure (cell diameter).

It is clear that, compared to the CO_2 blowing, the HCFCs give advantages in terms of thermal conductivity even over a very long period of time. For an 80mm thick XPS board, blown with HCFC-142b, the mean thermal conductivity over 25 years is between 20 and 30% lower than for a CO_2 board (depending on the

CO_2 board type) ; Over 100 years, its thermal conductivity is still lower by 14 and 24%!

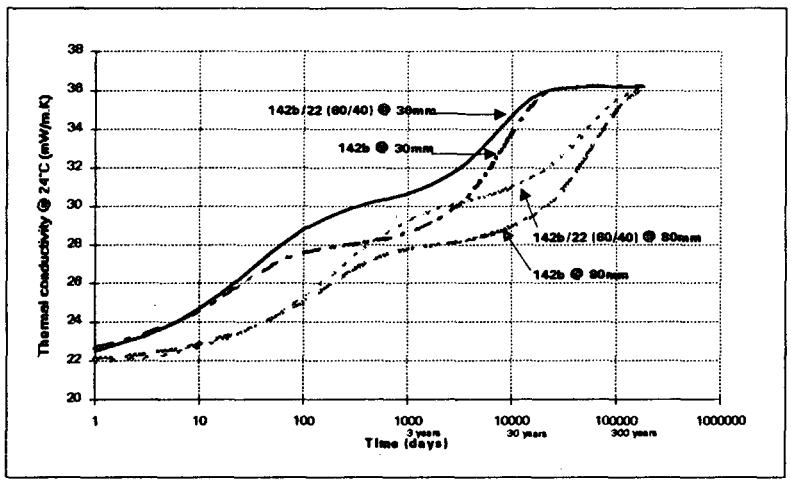


Figure 5. Effects of blowing agents and sample thickness on aging

Table 3. Effects of blowing agents and sample thickness on the aged thermal conductivities of XPS boards

Blowing agent	XPS board thickness (mm)	XPS board initial thermal conductivity (mW/m.K @ 24°C)	Mean thermal conductivity (mW/m.K @ 24°C) over					
			1 year	5 years	10 years	25 years	50 years	100 years
142b/22 (60/40)	30	21.8	29.2	30.6	31.2	32.6	34.0	35.1
142b/22 (60/40)	80	21.8	26.2	28.8	29.4	30.1	30.8	31.6
142b	30	22.1	27.6	28.7	29.3	31.0	32.9	34.5
142b	80	22.1	25.8	27.5	27.8	28.3	28.8	29.8
CO_2	no effect	34 - 37	34 - 37	34 - 37	34 - 37	34 - 37	34 - 37	34 - 37

ENVIRONMENTAL ACCEPTANCE OF HFCs AS BLOWING AGENTS FOR XPS INSULATING BOARDS

Despite their very good performance as blowing agents for XPS boards, HCFCs will have to be ultimately phased-out due to their ODP. Today, especially in Europe, two classes of zero ODP substitutes are competing. They are liquid CO_2 and HFCs.

Using liquid CO_2 as the blowing agent for XPS insulating boards result in some major drawbacks. First of all, CO_2 is very difficult to process and requires significant changes in the production equipment because of its high pressure. It may even require chemical modification of the polystyrene resin. This means more investment and higher cost. Moreover, CO_2 blown XPS boards suffer from serious degradation of the thermal conductivity, as indicated in the simulation. Finally, there is difficulty in obtaining low density and/or high thickness boards with CO_2. These may explain why CO_2 blowing is still an exception in Europe today, even among the companies which have already implemented the CO_2 technology. They are still using HCFCs for the main part of their production. HFCs are therefore more promising blowing agents, even though this option is also likely to demand some development work.

Before looking further into that possibility, one must be sure of the environmental acceptance of those HFCs as blowing agents for XPS insulating boards. There is a concern that HFCs contribute to the so-called greenhouse effect. This issue has already been addressed in numerous papers such as one by Libre [9]. Table 4 presents the projected radiative forcing for the year 2010 for different trace gas according to the IS92a scenario

from the International Panel on Climate Change (scenario often called "business as usual").

Table 4. Projected radiative forcing of trace gases

Trace gas	Corresponding radiative forcing (W/m^2) for the year 2010
CO_2	2.23
N_2O	0.2
CH_4	0.56
CFCs and HCFCs	0.3
HFCs	0.02
Total:	3.31

In 2010, carbon dioxide, generated by the burning of fossil fuels, will be by far the largest contributor to the global warming. The contribution of HFCs (among which HFC-134a will be the most predominant one) will be around 0.6%. Figure 6 represents the same scenario throughout the year 2100.

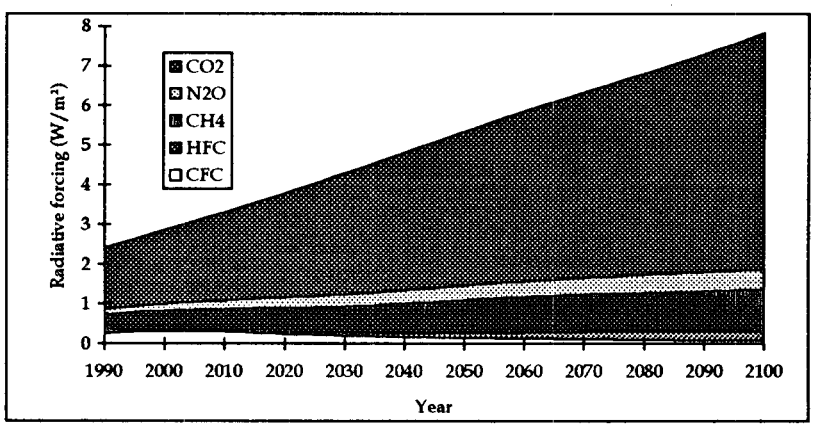


Figure 6. Predicted radiative forcing of compounds

Even with the very high and unrealistic HFCs' emission values retained for this scenario, their contribution to the global warming in 2100 would still be around 2.6%. More likely atmospheric release rate would result in a contribution lower than 1%. It is not possible to pinpoint the HFCs contribution to the greenhouse effect as other than insignificant.

If one still wishes to take into account the HFCs contribution to the global warming, it is necessary to look not only at their direct contribution but also at their indirect one, i.e. to look at their Total Equivalent Warming Impact (TEWI). This is a very important concept since insulation foams may have a direct impact on the global warming through the release of the blowing agent. They also have an indirect effect since that, depending of the foams' efficiency, the insulated house or warehouse will need more or less energy to maintain certain temperatures. The energy produced by the burning of fossil fuels liberates CO_2 into atmosphere (see figure 7).

An XPS board with a better thermal efficiency such as those blown with HCFCs is therefore more likely to give a better TEWI value than that of a CO_2 blown XPS board. Because of their long life expectancy within the foam cells, we can expect that HFCs will also lead to better TEWI values than CO_2 blown XPS boards, and therefore have a positive effect towards the reduction of the emission of greenhouse gases.

Another environmental issue that has also been raised against HFC-134a is that its atmospheric breakdown is likely to produce trace quantity of trifluoroacetic acid (TFA). However, it has already been clearly established that "these predicted concentrations and deposition fluxes (of TFA) are orders of magnitude smaller than what is thought to be toxic for humans, for the fauna, and for the flora" [10].

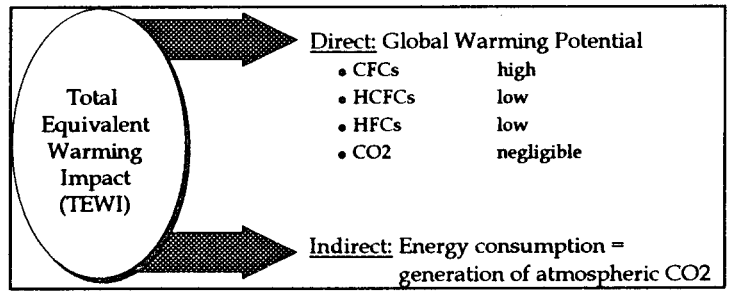


Figure 7. Direct and indirect global warming

TECHNICAL ACCEPTANCE OF HFCs AS BLOWING AGENTS FOR XPS INSULATING BOARDS

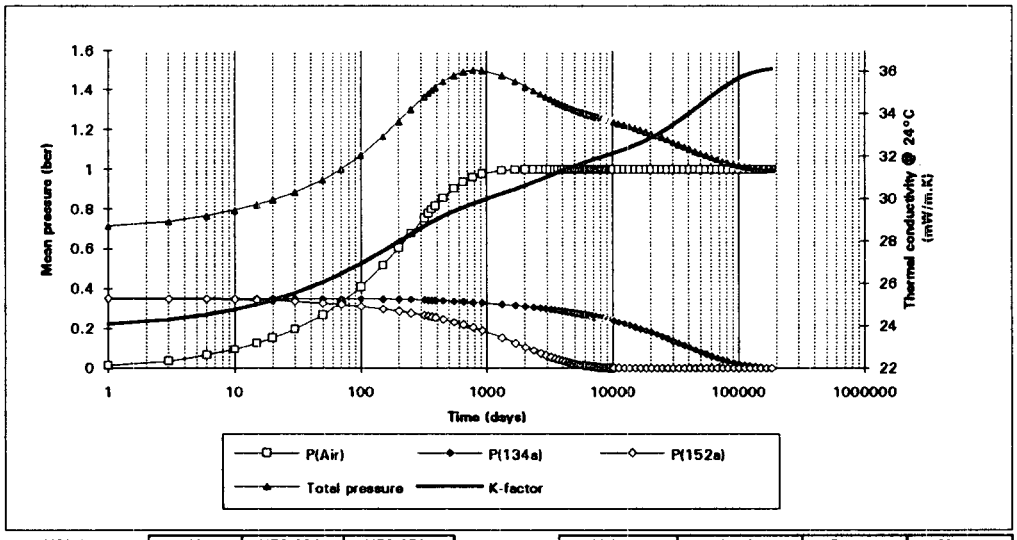
In the previous sections, we have shown that HFCs are environmentally acceptable. We now focus on their technical acceptance in that application.

The most significant technical difference between HFCs and HCFCs is their solubility in the molten polystyrene. It appears that HFC-134a has a lower solubility in polystyrene compared to HCFCs [4], and therefore may not be easily used as the sole blowing agent in the production of low density XPS insulating boards. Blending HFC-134a with other molecules such as HFC-152a or ethyl chloride could be a solution to this issue : the HFC-134a for the long term insulation and the co-blowing agents (HFC-152a, ethyl chloride,...) for the processability.

There is a need to have an accurate estimation of the diffusion rates of those zero ODP blowing agents in an XPS board. Some data were already presented in table 2. The data gathered for CFC-12 or the HCFCs were quite consistent. However, there are discrepancies among those for HFC-134a and HFC-152a. In the case of HFC-152a the permeability of HFC-152a lies between HCFC-22 and HCFC-142b, as observed by Suh et. al. [5]. However, Boy found that diffusion of HFC-152a is roughly ten times as high as the HCFC-22 [6]. Actual measurements on commercially available HFC blown XPS boards clearly show that the diffusion rate of HFC-152a lies in fact between HCFC-22 and HCFC-142b. A very first guess would lead to an effective diffusion coefficient of approximately 4×10^{-12} m^2/s for HFC-152a through an XPS board. As for HFC-134a, since it will remain much longer inside the XPS board, it's difficult to have an accurate estimation of its effective diffusion coefficient. Values from table 2 seem to suggest that the diffusion rate of HFC-134a is around or slightly higher than the one of HCFC-142b according to [4] and [5]. Obviously, a clarification of this point will be needed in the future.

Figure 8 shows the simulated k-factors of an HFC-134a/HFC-152a blown XPS board. The initial blend chosen for the simulation was HFC-134a/HFC-152a 60/40 by weight, equivalent to 50/50 by volume; The foam's structural parameters were the same as previously. As stated before, the effective diffusion coefficient used for HFC-152a is likely to be close to its real value whereas, in the absence of experimental data, the effective diffusion coefficient of HCFC-142b was chosen for HFC-134a.

Besides the uncertainty regarding the diffusion coefficient of HFC-134a, we would like to point out that the use of these new blowing agents could also alter the foam's structure (, i.e., a smaller cell diameter for the boards blown with a blowing agent that has a lower solubility in the melt). Finally, It should be noted that the blend of HFC-134a/HFC-152a, 60/40 by weight, used in the previous simulation would be flammable since the maximum amount of HFC-152a to keep the blend non-flammable is around 10 % by weight.



XPS foam	Air	HFC-134a	HFC-152a
Pressure	0.01	0.35	0.35
Diff. Coeff. (m^2/s)	3.00E-11	2.00E-13	4.00E-12

thickness (mm)	density (g/l)	diameter (microns)	Vstrut (%)
80	30.3	250	13

Figure 8. Simulation of aging of HFC-134a/HFC-152a XPS foam

CONCLUSION

HCFC-142b has been the substitute that had allowed a total CFC-12 phase-out while keeping the XPS insulating boards with good insulation properties. There is no doubt that HCFC-142b itself will be eventually replaced by blowing agents with zero ODP. . Among them, CO_2 and HFCs, especially HFC-134a, are so far the most promising candidates. The CO_2 blown XPS boards suffer from not only poor processability but also low thermal efficiency. On the other hand, with HFC-134a, it should be possible to retain most of the properties of the current XPS insulating boards. Certainly, work needs to be done regarding the foaming of XPS boards with HFC-134a (alone or in blends). Here lies the challenge that will face the XPS insulating board industry in the coming years.

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BIOGRAPHICAL NOTES

Jean-Denis ROUX is an Engineer with Elf Atochem S.A. based at their Application Laboratory. Since 1992, he has been in charge of the FORANE range development/technical service in the area of blowing agents for cellular plastics.

Arnaud ALBOUY graduated in 1993 from the Ecole Superieure de Physique et Chimie Industrielles de la Ville de Paris. He joined Elf Atochem in 1995. His current responsibilities are the development of blowing agents for plastic foams.

Denis MOUTON has been working on plastic foams for the last 25 years. He joined Elf Atochem in 1989 as a business manager in charge of the FORANE (blowing agents/solvents).

Jinhuang WU is a scientist at Elf Atochem North America's Technological Centre in King of Prussia. He received his Ph.D. in Macromolecular Science and Engineering from the University of Michigan and joined Elf Atochem in March 1997.

REFRIGERATOR FOODLINERS
VS.
NEXT GENERATION FOAM BLOWING AGENTS
PLASTIC/FOAM COMPATIBILITY III

KENNETH L. HORTIN
WHIRLPOOL CORPORATION
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EVANSVILLE, INDIANA 47727-0001

REPRESENTING
THE APPLIANCE INDUSTRY/GOVERNMENT CFC REPLACEMENT CONSORTIUM
(AHAM - APPLIANCE RESEARCH CONSORTIUM)

ABSTRACT

HCFC 141b (non-fully halogenated hydrochlorofluorocarbon) blown foams are currently used successfully with foodliners produced from selected grades of either ABS (acrylonitrile-butadiene-styrene) or HIPS (high impact polystyrene). However, HCFC 141b blown foams will be phased out by 2003 due to their implication in depletion of the ozone layer.

Evaluations are currently underway within the Appliance Industry-Government Replacement Consortium (ARC) to develop alternate zero ozone depleting foam blowing agents to replace HCFC 141b. ARC has previously sponsored two projects to evaluate the effects of HCFC blown polyurethane foams on ABS, HIPS and other potential alternate plastic materials.

This paper will review the details of a third study with alternate plastic materials to determine the effects of zero ozone depleting foams.

It is important to note that this evaluation is a materials screening test only and not intended to demonstrate actual performance of foodliners produced from the various alternate plastic materials.

BACKGROUND

Consortium project participation

In 1989, several of the refrigerator / freezer manufacturer members of the Association of Home Appliance Manufacturers (AHAM) with the encouragement and in cooperation with the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Energy (DOE) incorporated the Industry / Government CFC Replacement Consortium, Inc. (also called the Appliance Research Consortium). The Consortium was established to develop non-CFC replacements for CFC 12 used as a refrigerant and CFC 11 used as a blowing agent for polyurethane insulating foams. Insulation related developments are

coordinated by the Insulation Technical Advisory Committee (ITAC) and are supported by the following companies: *refrigerator / freezer manufacturers* - Amana, Frigidaire, General Electric, Marvel, Maytag, Sanyo, Sub-Zero, W.C. Wood, and Whirlpool; *blowing agent suppliers* - Allied-Signal, Dupont, Elf Atochem, Exxon Chemical and ICI; *foam chemical suppliers* - Air Products, Bayer, Dow, Goldschmidt Chemical and ICI; *plastic suppliers* - BASF, Bayer, Dow, Enichem and G.E. Plastics.

Previous project activity

Two previous plastic / foam compatibility projects have been completed within the ITAC. The first project entitled Refrigerator Food Liners vs. HCFC Foams (reported at the 42nd International Appliance Technical Conference at Madison in 1991) focused on general compatibility of industry standard grades of Acrylonitrile-Butadiene-Styrene (ABS) and High Impact Polystyrene (HIPS) vs. HCFC 123 and HCFC 141b blown foam insulation. **The results of this test indicated that improvements in the chemical resistance of ABS and HIPS were necessary for use with HCFC blown foams.**

A second project entitled Refrigerator Foodliners vs. HCFC Foams, Plastic / Foam Compatibility II, (reported at the 44th International Appliance Technical Conference at Ohio State in 1993) focused on alternate plastic materials designed to withstand chemical attack from HCFC blown foams. **The results of this study indicated that some potential better plastic material options were available for use with HCFC blown foams although careful large scale trials would be necessary before any of the options could be judged acceptable for production.**

Current plastics used with HCFC foam

Foodliners produced from selected grades of either ABS or HIPS are currently used successfully with HCFC 141b (non-fully halogenated hydrochlorofluorocarbon) blown foams. In some cases the plastic liner materials are produced by the coextrusion process which incorporates a plastic barrier layer.

HCFC future phaseout

HCFC 141b, currently used as a foam blowing agent, is viewed by the EPA as a transition material until an energy efficient, zero ODP (ozone depletion potential) blowing agent is commercially available. The deadline for replacement of HCFC 141b is December 31, 2002. Plastic food liner materials compatible with zero ODP blown foams must be developed within this time frame as well.

Zero ODP blowing agent candidates

Due to their chemical characteristics, the following HFC (hydrofluorocarbon) materials have been determined to be potential foam blowing candidates to replace HCFC 141b: HFC 134a, HFC 236ea and HFC 245fa. Also, cyclopentane was added to the blowing

agent evaluation list due to its availability and current usage in several countries. These blowing agents were selected for use in this Plastic/Foam Compatibility III project.

Project Participation

The following Appliance Manufacturers, Foam Suppliers, Plastic Suppliers and Blowing Agent Suppliers participated in this project which was completed during 1996:

APPLIANCE MANUFACTURERS

MAYTAG	FRIGIDAIRE	SANYO	W. C. WOOD
AMANA	GENERAL ELECTRIC	SUB-ZERO	WHIRLPOOL

PLASTIC SUPPLIERS	PLASTIC SUPPLIERS	BLOWING AGENT SUPPLIERS
DOW CHEMICAL	BASF	ALLIED SIGNAL
G.E. PLASTICS	DOW CHEMICAL	ELF-ATOCHEM
BASF	ICI	DUPONT
BAYER	BAYER	ICI
ENICHEM		EXXON CHEMICAL

Test Method

As in the previous two projects, a foamed refrigerator fresh food door assembly (Figure 1) was utilized as the test vehicle to screen the alternate plastic material candidates. The door assembly consists of a thermoformed plastic inner door liner attached to a steel outer door and then foamed-in-place with various foams. This steel/foam/plastic sandwich construction was previously determined to provide significant design shape factors and would be of sufficient size to simulate food liner thermal strains. A test plan was developed and executed which would demonstrate the severity of the next generation foam attack on these alternate plastic materials.

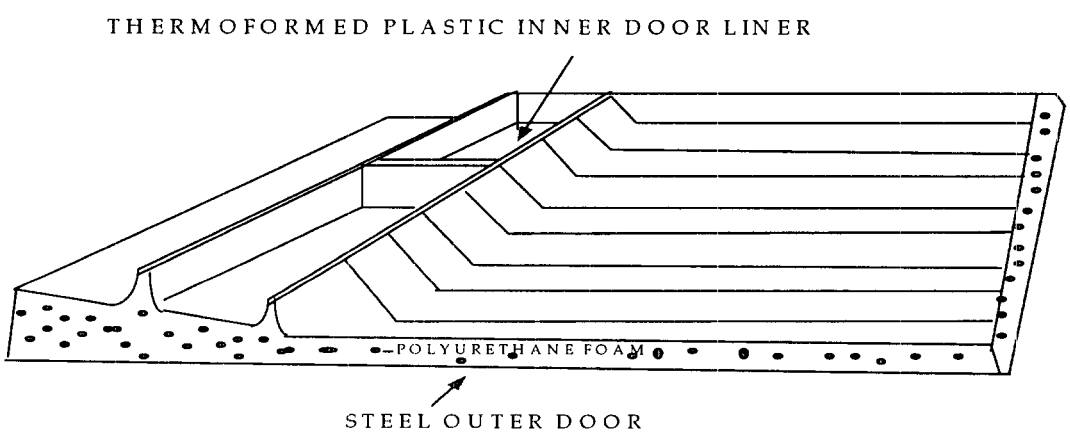

Figure 1

Plastic Door Liner Preparation

Each participating plastic material supplier forwarded 30 pieces of extruded sheet stock (41"x53"x0.075") to a central location for inner door liner thermoforming, trimming, hole piercing and attachment to steel outer doors via screws and metal retainer strips. A total of 12 different plastic candidates were submitted from five plastic suppliers. Each of the plastic materials were coded for confidentiality. No release agents were applied to the surfaces of the plastic or steel. As in the previous studies, special protective shipping cartons were utilized for shipment to foaming locations and final evaluation sites.

Foamed Door Preparation

The best available HCFC 141b, C-pentane, HFC 134a, HFC 236ea and HFC 245fa blown polyurethane foam systems were used in the preparation of the test door assemblies in accordance with the following plan:

Foam Type	Coded Liner Material (4 each)	Total Doors
1. HCFC 141b (base)	1, 2, 3, 4, 5, 6	24
2. HFC - 245fa	7,8,9,10,11,12,13,14	32
3. C-Pentane	15,16,17,18,19,20,21	28
4. HFC - 236ea	22,23,24,25,26,27,28	28
5. HFC - 134a	29,30,31,32,33,34,35	28
		140 Grand Total

Prior to the foaming process, liner fixtures and support plugs and fixtures were forwarded to the three foaming locations. After foaming completion, the foamed door assemblies were forwarded to four different locations for thermal performance testing.

DOORLINER THERMAL TESTING

The Test Protocol

As in the previous two projects, the door assemblies were submitted to temperature extremes of 140°F and -20°F for hold times of 8 hours with a transition time of 2 hours between each temperature extreme. Ten cycles were completed and the doorliners were inspected at room ambient temperature at the completion of each cycle. A three day stabilization at 110°F was used at the beginning of the test to attempt to normalize the heat history of the doors. One assembly from each group of four was used as a control (not subjected to thermal cycling) for impact and adhesion testing for comparison to the thermal cycled assemblies.

Although a mixture of cottonseed oil and oleic acid (simulating food contamination) is frequently used to approve liner materials and liner designs, it was not used in this test protocol since the objective of this test was to evaluate only foam and blowing agent effects.

A total of 35 controls were held at ambient and 105 doors were subjected to thermal cycling at four different sites.

Inspection Recordkeeping

Each door was inspected at the start of testing and at the completion of each cycle. Failure type, location and size were recorded on a door drawing and a tally sheet.

Thermal Cycle Test Summary

Figures 2 - 6 show the total cracking frequency per group of three doors for each plastic material and each blowing agent.

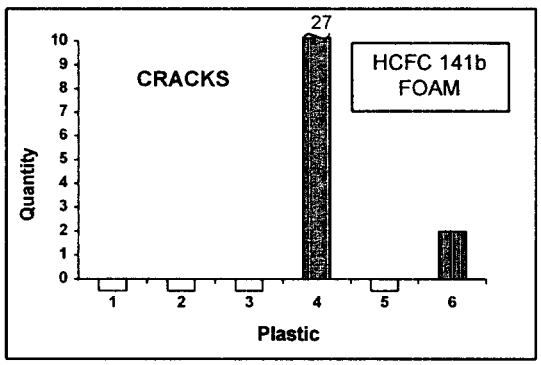

Figure 2

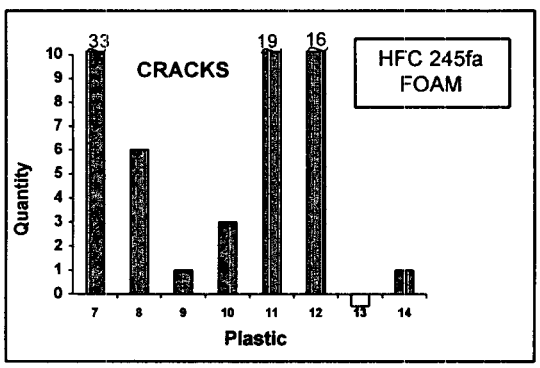

Figure 3

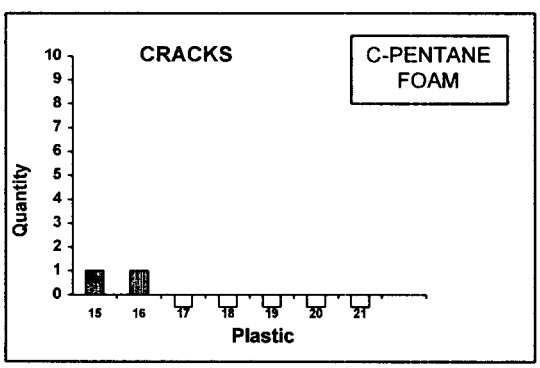

Figure 4

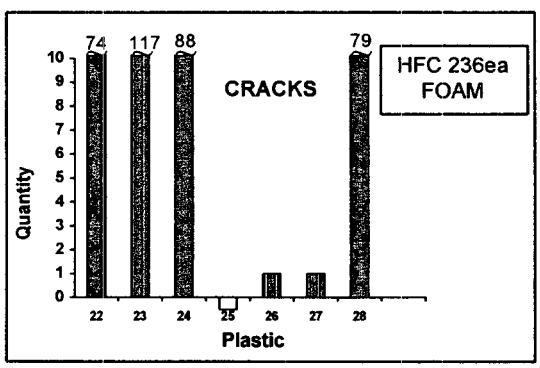

Figure 5

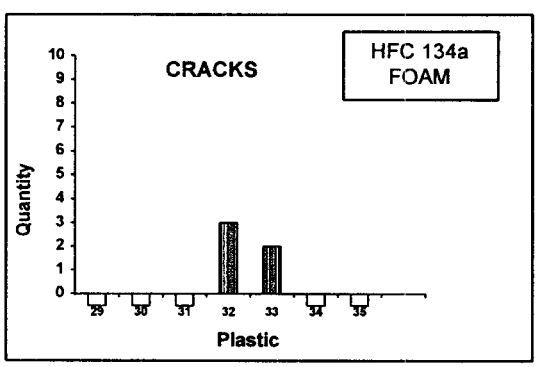

Figure 6

Blister Test Summary

Figures 7-11 shows the total blistering frequency per group of three doors for each plastic material and each blowing agent.

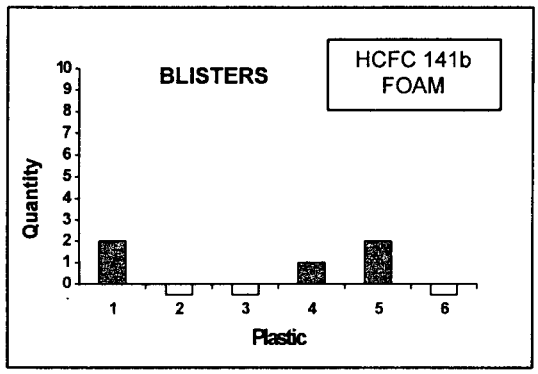

Figure 7

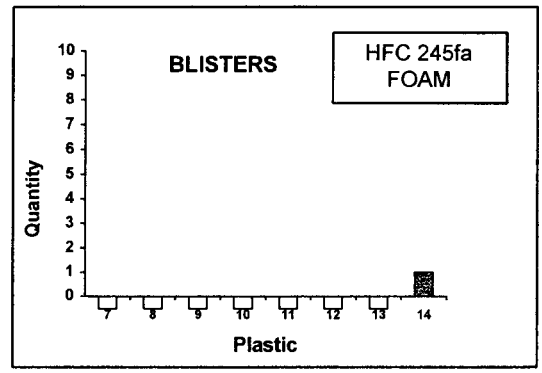

Figure 8

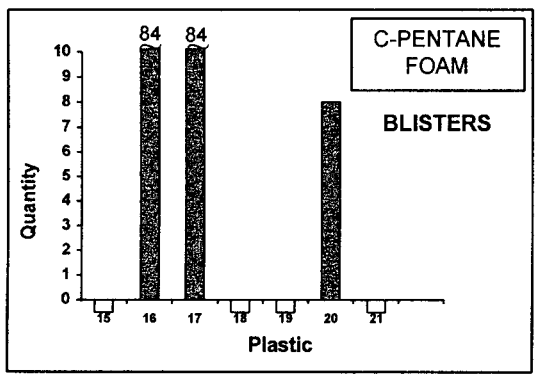

Figure 9

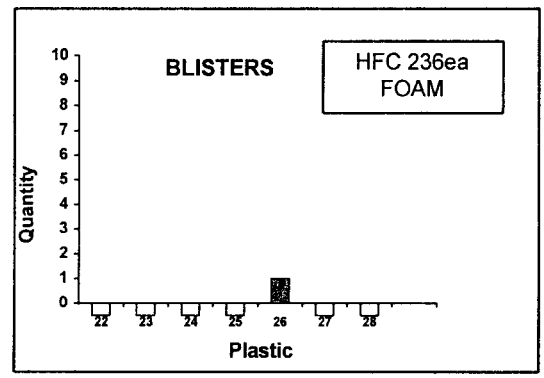

Figure 10

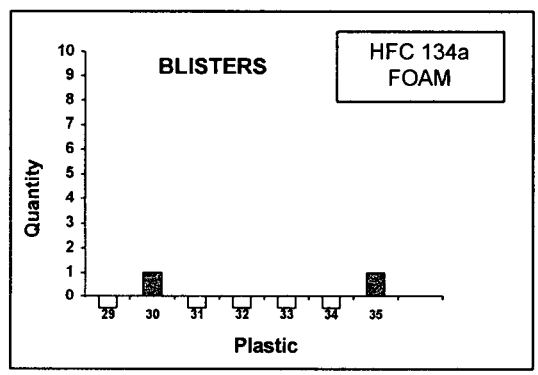

Figure 11

INSTRUMENTED TESTING OF CYCLED AND NON-CYCLED DOORS

Test Methodology

Six inch by six inch impact test specimens were cut from the flat vertical portion of the assemblies consisting of the steel, foam, plastic composite as shown in Figures 12 and 13. The test specimens were impact tested in a laboratory standard dart drop instrument at a temperature of 72°F.

Impact and adhesion testing was conducted on one control assembly and one thermocycled assembly from each foam and plastic combination.

The instrumented impact tester is designed to evaluate materials strength under conditions of dynamic loading. Specimen resistance is measured by a force transducer mounted to the falling weight. The total energy absorbed is a calculated value and is a function of a material's strength and ductility.

Foam adhesion specimens were prepared by carefully cutting two inch wide sections from the vertical portions of the top shelf area of the assemblies as shown in Figure 12. Adhesion values were obtained in 90 degree (perpendicular) peel tests using a standard laboratory tensile test machine.

SPECIMEN LOCATION

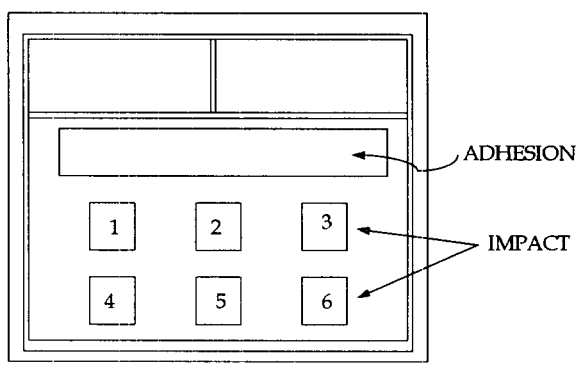

Figure 12

IMPACT SPECIMEN

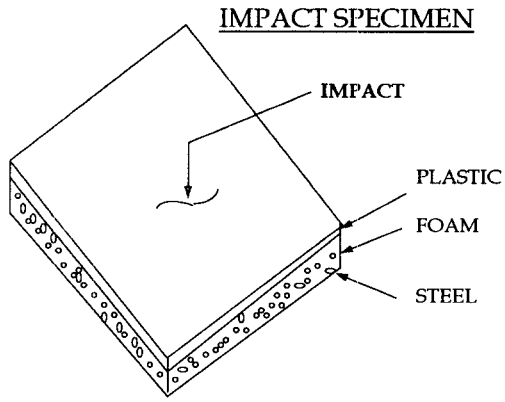

Figure 13

Instrumented Impact Evaluation Results

Impact tests were conducted on 6 specimens from each plastic and foam combination before and after thermocycling with results statistically compiled. The test results are shown graphically in Figures 14-18 for each type of plastic and foam.

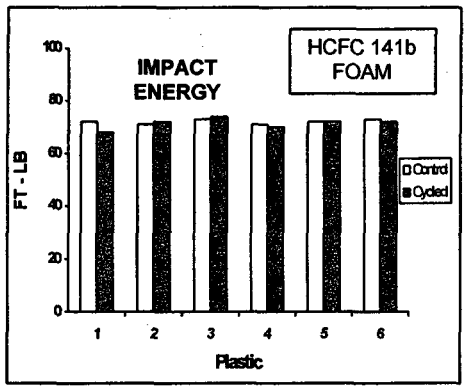

Figure 14

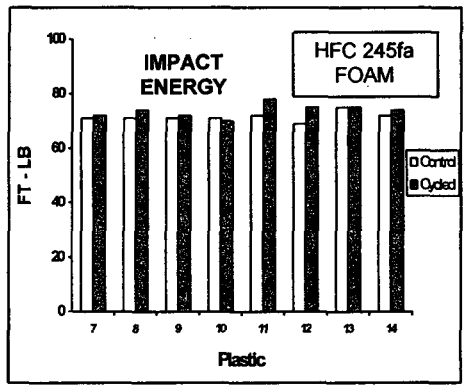

Figure 15

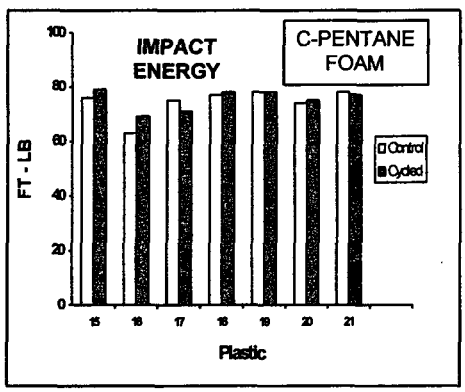

Figure 16

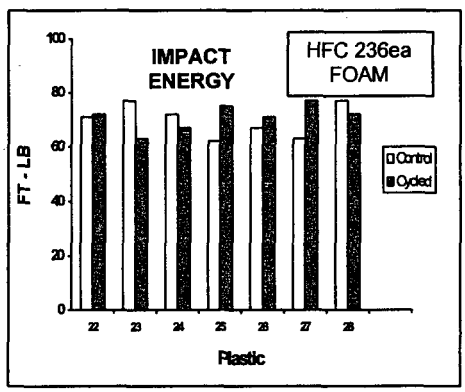

Figure 17

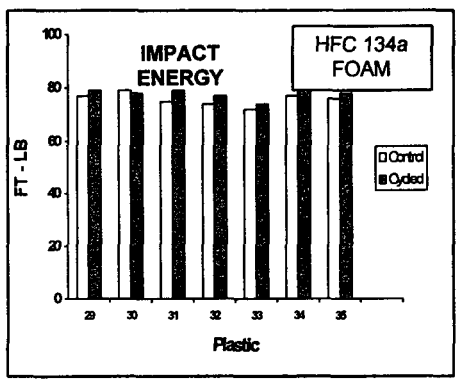

Figure 18

Adhesion Evaluation Results

Peel adhesion tests were conducted on one specimen from each plastic and foam combination before and after thermocycling. Results revealed a mixture of adhesive and cohesive failures at the plastic and foam interface depending on the specific plastic and foam type. Peel test values are shown graphically in Figures 19-23.

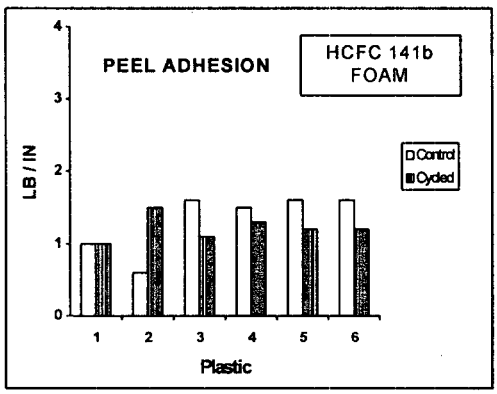

Figure 19

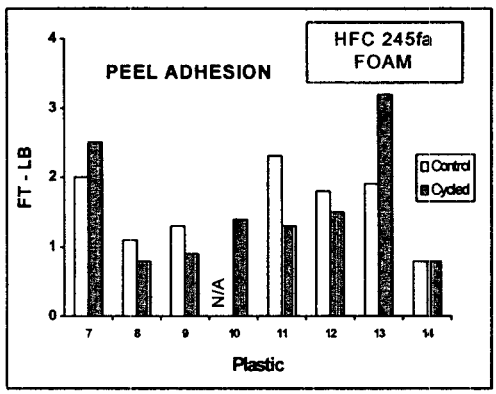

Figure 20

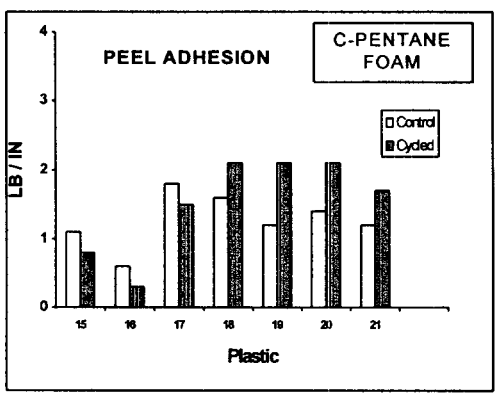

Figure 21

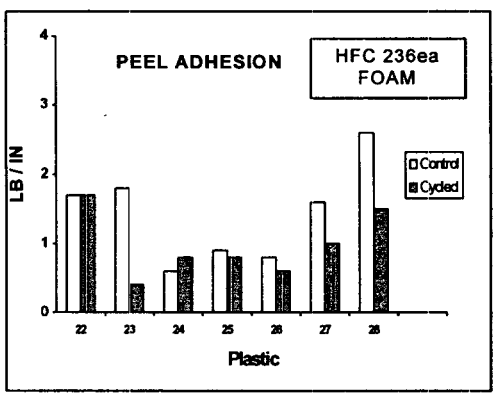

Figure 22

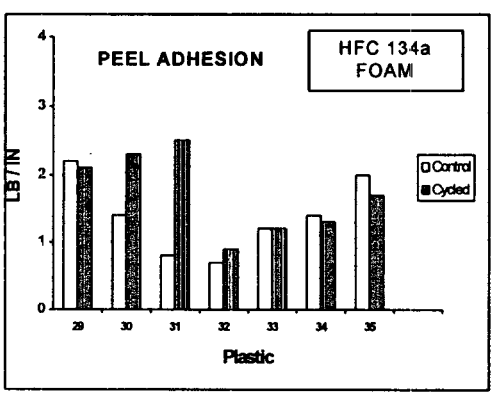

Figure 23

GENERAL OBSERVATIONS AND CONCLUSIONS

The test results of this third foam/plastic compatibility evaluation indicate there are promising plastic material options for each of the five types of foams evaluated. The incidence of cracking and blistering ranged from extensive to slight to none depending on the specific plastic and foam combination. The impact values showed less distinction between types of foam and plastics. No conclusions could be drawn on adhesion levels due to the wide range of values obtained.

While these results indicate that there may be one or more plastic options based on the type of foam used, pilot runs of a larger scale would be necessary before any of these materials could be approved for commercial production. Pilot runs would address other very important issues such as processing parameters, color stability, regrind compatibility, etc. which are also necessary to qualify a material for production use.

Future Plans

Currently, there are no scheduled follow on test programs for plastic and foam compatibility. The extent of any future programs will be decided pending the commercial success of the materials evaluated thus far and the industry needs to generate additional studies.

Acknowledgments

The author gratefully acknowledges support and guidance from the appliance manufacturers and suppliers who made major contributions to this test program through participation in the protocol development and financial or in kind support.

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AGING OF POLYURETHANE FOAM INSULATION IN SIMULATED REFRIGERATOR WALLS

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ABSTRACT

Laboratory data are presented on the thermal conductivity[1] of polyurethane foam insulation in composite test panels that simulate refrigerator walls. The test panels consisted of a steel skin, an ABS plastic liner, and a polyurethane foam core. Foam cores were produced with three different blowing agents (CFC-11, HCFC-141b, and a HCFC-142/22 blend). Periodic thermal measurements have been made on these panels over a three and one-half year period in an effort to detect aging processes. Data obtained on foam encased in the panels were compared with measurements on thin foam slices that were removed from similar panels. The data show that the encapsulation of the foam in the solid boundary materials greatly reduces the aging rate. The plan is presented for a follow-on project that is being conducted on the aging of foams blown with HCFC-141b, HFC-134a, HFC-245fa, and cyclopentane.

INTRODUCTION

In July of 1991, a Cooperative Research and Development Agreement (CRADA) was signed between the Appliance Industry-Government CFC Replacement Consortium (also known as the Appliance Research Consortium, or ARC) and the Oak Ridge National Laboratory. One phase of that CRADA involved the aging characteristics of polyurethane foam insulation produced with second-generation blowing agents. While that CRADA was concluded in 1996, studies of the aging characteristics of second-generation blowing agents have continued. With support from the U. S. Department of Energy, the U. S. Environmental Protection Agency, and the Appliance Research Consortium, a similar, but more detailed, study has been started on the aging characteristics of polyurethane foam insulation blown with third-generation blowing agents.

SPECIMENS

Specimens for the aging studies were fabricated as panels that simulate the construction of a door or wall of a refrigerator. The panels were about two inches thick and were bounded by a sheet of 24 gauge (0.024 inch thick) steel on one side and by a 0.12 inch thick sheet of acrylonitrile-butadiene-styrene (ABS) plastic on the other side. The steel sheet represents the outside of a refrigerator cabinet, while the plastic sheet represents the inside lining. The space between the two sheets was filled with polyurethane foam. The lateral dimensions of the panels were 24 by 24

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[1] Since heat transfer through foam insulation is a combination of conduction and radiation, the term "apparent thermal conductivity" is sometimes preferred. In this paper, the term "thermal conductivity" is used for simplicity.

inches, and the edges of the panels were sealed with aluminum foil tape to simulate the configuration in a refrigerator where there are no cut, exposed foam edges.

The panels were fabricated by three foam suppliers, each of which used a different foam blowing agent. The three types of blowing agents used were CFC-11, HCFC-141b, and a HCFC-142b/22 blend. The CFC-11 panels were intended to represent a base case with which the second-generation blowing agents could be compared. These panels were fabricated around the end of 1993, and at that time foams produced with second-generation blowing agents had not been optimized. Hence the results obtained on specimens blown with the second-generation blowing agents are not necessarily representative of current capabilities.

In addition to the panel specimens, core foam specimens were prepared by removing the foam from panels, cutting out 12 inch squares, and then slicing them. Typical slice thicknesses were about 0.35 and 1.5 inches. A stack of four of the 0.35 inch-thick slices made up one test specimen.

EXPERIMENTAL PROCEDURES

Thermal resistance measurements were made using two heat-flow-meter-apparatuses (HFMAs), which conform to ASTM C 518.[1] Tests on the core foam specimens were made in a HFMA that accepts specimens up to 12 inches square, while tests on the panels were made using a HFMA that accepts specimens up to 24 inches square. For the tests on the panels, intervening layers of foam rubber were placed between the panel and the hot and cold plates of the apparatus to eliminate any undesirable air gaps between the specimen and the plates and also to protect the plates from the rigid test panel. Thermocouples were taped directly to the faces of the test panels so that the temperature difference across the test panel was measured directly. Since the measurements gave the overall thermal resistance of the test panel, a correction was made for the thermal resistances of the steel and plastic sheets to obtain the thermal conductivity of the foam insulation. Tests on the core foam specimens gave the thermal conductivity directly.

All HFMA tests were performed with the hot and cold plates maintained at 95°F and 55°F, respectively, giving a mean temperature of 75°F. During the time periods between thermal tests, the specimens were stored in closed atmospheric pressure aging chambers that were maintained at a constant temperature of 90°F.

RESULTS AND DISCUSSION

Thermal conductivity measurements were made on the core foam specimens over a period of 180 days. The specimens were sliced soon after the foam was blown, and the aging period started immediately after the specimens were sliced to their test thicknesses. Results are shown in Figure 1, where the thermal conductivity is plotted versus the square root of the aging time divided by the slice thickness ($\sqrt{t}/L$). The data are seen to be divided into two nearly linear regions. The first region is associated with the diffusion of air into the cells of the foam, while the second region is associated with the diffusion of the blowing agent out of the cells. The lines on Figure 1 were obtained from linear regressions of the logarithm of the thermal conductivity [*ln* (100 k)] versus

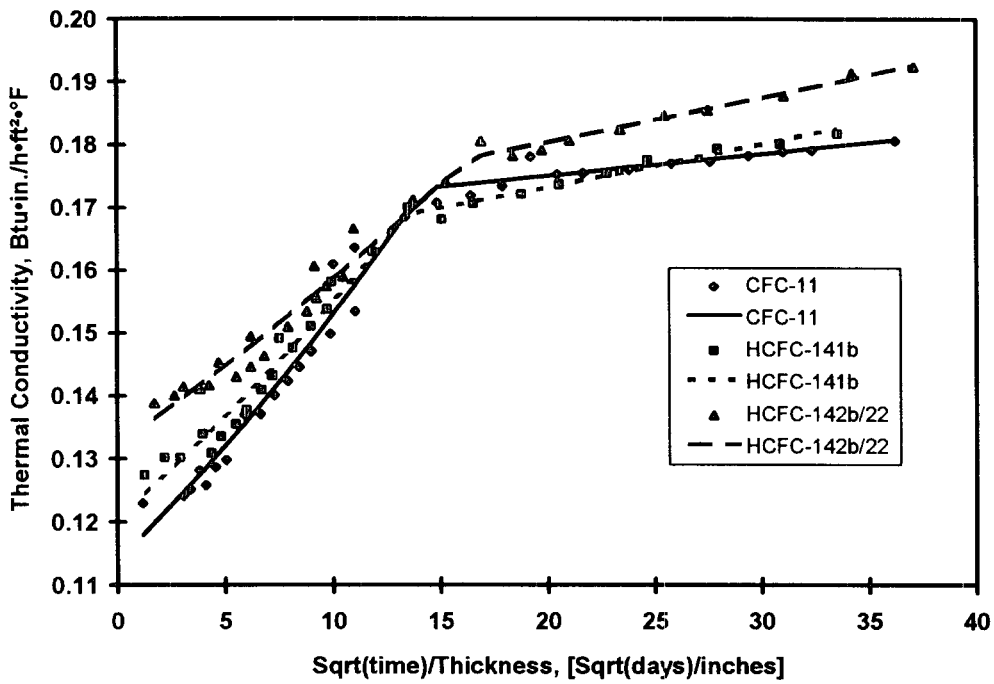

Figure 1. Thermal Conductivity of Core Foam Specimens

the square root of the aging time divided by the slice thickness ($\sqrt{t}/L$). This type of relationship has traditionally been used in the past, but as can be seen in Figure 1, the curves are nearly linear when the thermal conductivity is plotted versus the same time-thickness parameter. At short times, the conductivity of foam blown with HCFC-141b is about 5 to 6 percent higher than that of foam blown with CFC-11, and the values for HCFC-142b/22 are about 15 to 16 percent higher than those for CFC-11. At long times, the differences among the blowing agents are diminished. The long-time conductivity for HCFC-141b is about 3 to 4 percent higher than that for CFC-11, and the values for HCFC-142b/22 are about 7 percent higher.

Thermal measurements have been made on the full-thickness panels over a period of 3-1/2 years. Foam thermal conductivities obtained from these measurements are given in Table 1. As was the case with the thin-slice specimens, the initial thermal conductivities of the foam blown with second-generation blowing agents were higher than that for CFC-11. For the full-thickness panels, the conductivities were higher by about 16 and 11 percent for HCFC-141b and HCFC-142b/22, respectively. Again, it should be noted that these specimens were produced in late 1993/early 1994, and at that time the formulations for the HCFC blowing agents had not been optimized.

The foam thermal conductivities from the tests on composite panels are plotted versus aging time in Figures 2 through 4. The data on the core foam given in Figure 1 showed that, for each of the two phases of aging, the thermal conductivity is approximately a linear function of the square root

Table 1. Thermal Conductivity of Foam Insulation from Composite Test Panels

Blowing Agent	Aging Time, months					
	0	6	12	24	36	42
CFC-11	0.1158	0.1286	0.1192	-	0.1246	0.1234
"	0.1270	0.1129	0.1192	-	0.1226	0.1226
"	0.1087	0.1167	0.1217	0.1194	0.1254	0.1261
HCFC-141b	0.1369	0.1462	0.1409	-	0.1460	0.1510
"	0.1353	0.1473	0.1364	-	0.1469	0.1510
"	0.1362	0.1283	0.1368	0.1443	0.1450	0.1495
HCFC-142b/22	0.1311	0.1353	0.1372	-	0.1353	0.1369
"	0.1291	0.1326	0.1352	0.1298	0.1362	0.1337
"	0.1305	0.1317	0.1301	-	0.1336	0.1346

Note: Thermal conductivity values have units of Btu•in./h•ft²•°F.

of the aging time. Following this lead, the thermal conductivity data from the full thickness panels were fitted by the method of least squares to an equation linear in the square root of aging time. The solid lines in Figures 2 through 4 are the regression curves, and the dotted lines are the 95% confidence intervals derived from the regressions.[2] The dashed lines are the thermal conductivities calculated from the curves in Figure 1 for the core foam, with the time being scaled to correspond to the thickness of the foam in the full thickness panels.

As was expected, aging curves obtained only from measurements on core foam specimens cannot be used to predict the rate of aging of the foam in the panels. After 3-1/2 years, the thermal conductivity of the CFC-11 panel foam increased about 6 percent, while the core foam showed a 53 percent increase. Similar differences exist for the other two blowing agents. Clearly, encapsulation of the foam between the solid steel and plastic sheets and sealing of the edges with aluminum foil tape greatly decreases the rate at which gases can diffuse into or out of the cells of the foam. Core foam data, however, are valuable in that they provide information on the characteristics of the foam itself, while the aging behavior of panels depends upon the characteristics of both the foam and the bounding surface layers.

The regressions in Figures 2 through 4 are extended out to an aging time of 10 years. Admittedly, extrapolation far beyond the range of measured data is dangerous. This is especially true when

[2] Two types of intervals are used with regression analyses: confidence intervals and prediction intervals. Confidence intervals apply to the mean curve from the regression. Prediction intervals apply to an individual data point, and are wider than confidence intervals. Confidence intervals were chosen for use here, since our main interest is in the mean curve. For a discussion of these types of intervals, see a statistics textbook, such as Reference 2.

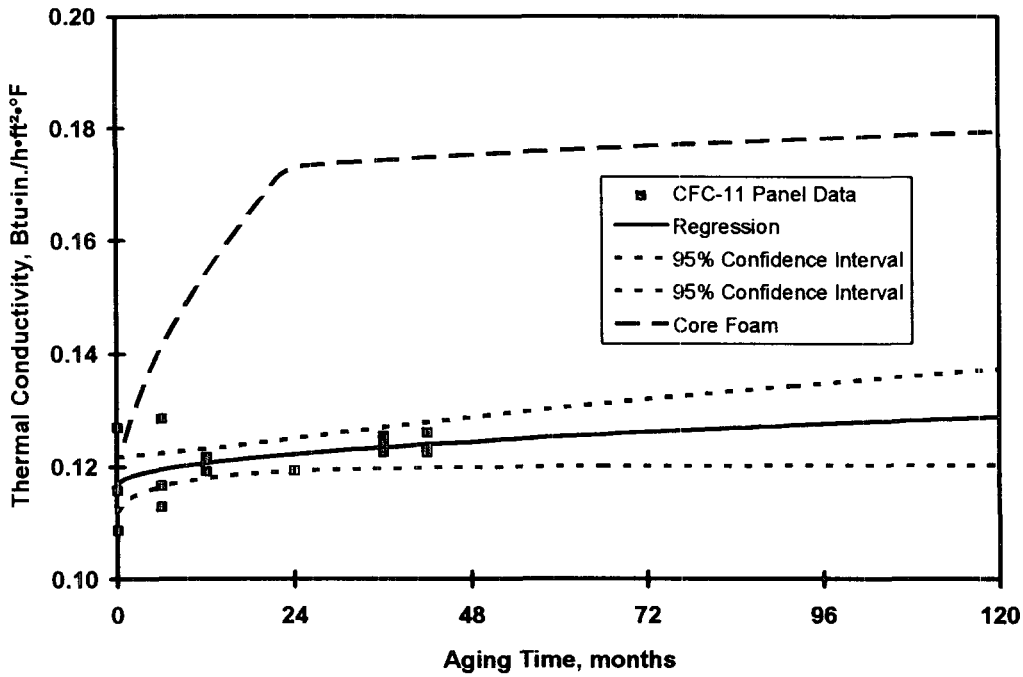

Figure 2. Thermal Conductivity of Foam Blown with CFC-11

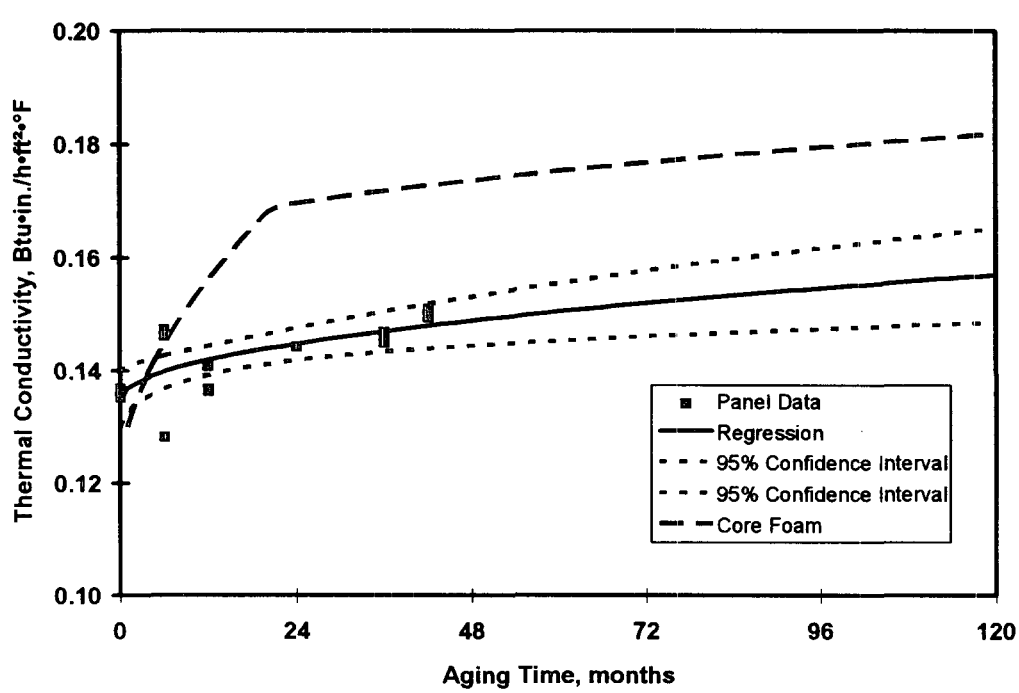

Figure 3. Thermal Conductivity of Foam Blown with HCFC-141b

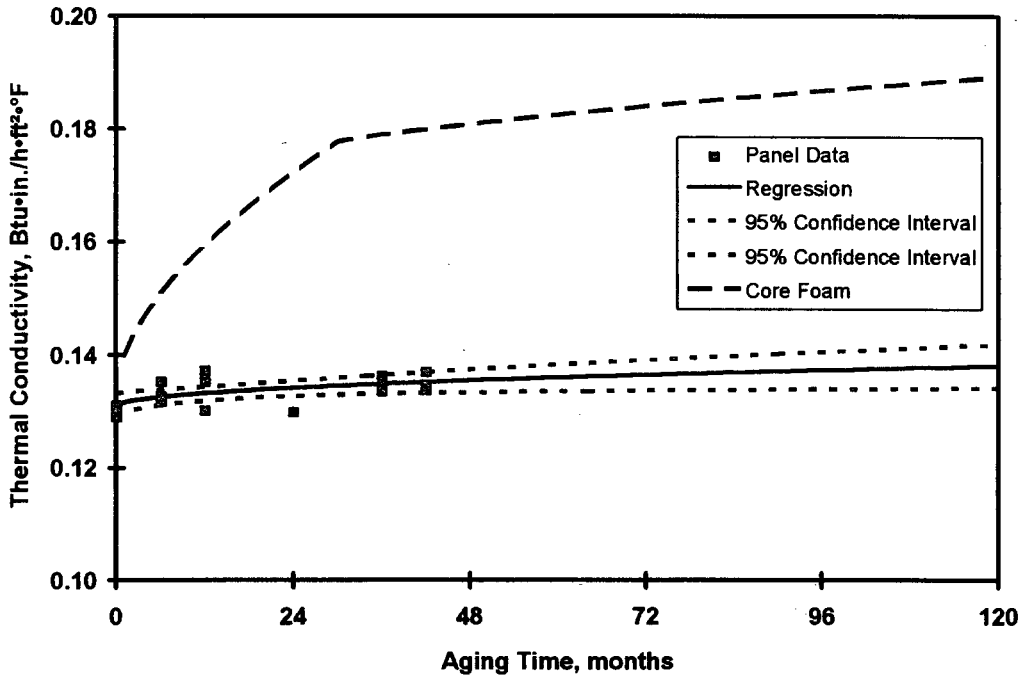

Figure 4. Thermal Conductivity of Foam Blown with HCFC-142b/22

the coefficients of determination (r^2) of the regressions are not large (they were 0.24, 0.52, and 0.35 for CFC-11, HCFC-141b, and HCFC-142b/22, respectively). However, it is very desirable to make some prediction of the long-term performance of the foam based on data obtained over a limited time period. Hopefully the true long-term performance will fall within the confidence intervals. The validity of these extrapolations will be determined as we continue to make measurements on these panels. Based on the 95 percent confidence intervals, the thermal conductivity of the foam blown with CFC-11 is expected to increase by 3 to 18 percent after aging for 10 years at 90°F. Conductivity increases for HCFC-141b and HCFC-142b/22 are expected to be 10 to 23 percent and 3 to 8 percent, respectively. There is an additional element of uncertainty in attempting to apply these changes to the insulation in operating refrigerators since the exposure temperatures would generally be lower than 90°F.

A mathematical model of foam aging was used to predict the change with time of the thermal conductivity of the foam in the composite panels. The one-dimensional model is similar to those described in the literature for diffusion of air and blowing agent through the foam.[e.g.,3,4] We have added the resistances to gas movement due to the finite permeances of the solid sheets on the surfaces of the panels. Given initial partial pressures of gases within the cells of the foam and the partial pressures of the gases surrounding the foam, the model calculates the time variation of the partial pressures within the cells. These partial pressures are used to calculate the thermal conductivities of the gas mixtures within the cells through the Lindsay-Bromley formulation of the Wassiljewa equation.[5] The various parameters needed for the model were taken from the literature and are given in Table 2. For the predictions given here, we have assumed that the only

Table 2. Parameters used in Model of Aging of Foam Insulation in Composite Test Panels

Gas	Thermal Conductivity at 75°F, Btu•in./h•ft²•°F	Effective Diffusion Coefficient at 90°F, cm²/s	Permeance of ABS Plastic, cc(STP)•mil/ 100 in.²•atm•day
N_2	0.178 [6]	0.043×10^{-6} [8]	21 [10]
O_2	0.179 [6]	0.28×10^{-6} [8]	125 [10]
CFC-11	0.058 [7]	0.0027×10^{-6} [9]	2.46
HCFC-141b	0.068 [7]	0.0050×10^{-6} [9]	1.34

Notes: Numbers in brackets are the references. Permeances of ABS plastic to the blowing agents were estimated by assuming the ratio of the permeance of the blowing agent to that of nitrogen to be the same as the ratio of the diffusion coefficients. The permeance of 24 gauge steel was taken to be zero.

gas initially within the cells is the blowing agent and that its initial partial pressure is 0.7 atmospheres.[3] In addition, we have not yet included any effects of condensation of the blowing agent, such as may occur with high-boiling-point blowing agents.

Figure 5 compares the predictions of the aging model with measured data and regressions of the data for the panels blown with CFC-11 and HCFC-141b. For these calculations, the aging model was forced to match the initial point of the regression curve at the beginning of aging. Figure 5 shows that the model is in good agreement with the regression curves. For both blowing agents, the shape of the model curves are very similar to the regression curves, and predict very similar increases in thermal conductivity. In both cases, the model curve is within a few percent of the regression curve. It should be emphasized that the only parameter in the model that we have adjusted to match the data is the initial thermal conductivity; all other parameters were taken from the literature. Better agreement might be obtained if the parameters that apply to the specific materials used in the panels were available. The good agreement between the model and the regression curves shows that the regression curves are physically realistic and gives some added credence to the extrapolations of the data to long time periods.

PLAN FOR THIRD-GENERATION BLOWING AGENT STUDY

The study of third-generation blowing agents will examine the effect of several factors on the aging characteristics of polyurethane foam. The first of these factors is, of course, the blowing agent itself. HCFC-141b will be used as a base case. Other blowing agents that will be studied are HFC-134a, HFC-245fa, and cyclopentane. At the present time, these three blowing agents are the only commercially available replacements for HCFC-141b. The second factor is the aging temperature. Three aging temperatures have been chosen: 90°F, 40°F, and -10°F. These temperatures span most of the range of temperatures to which the foam would be exposed in a

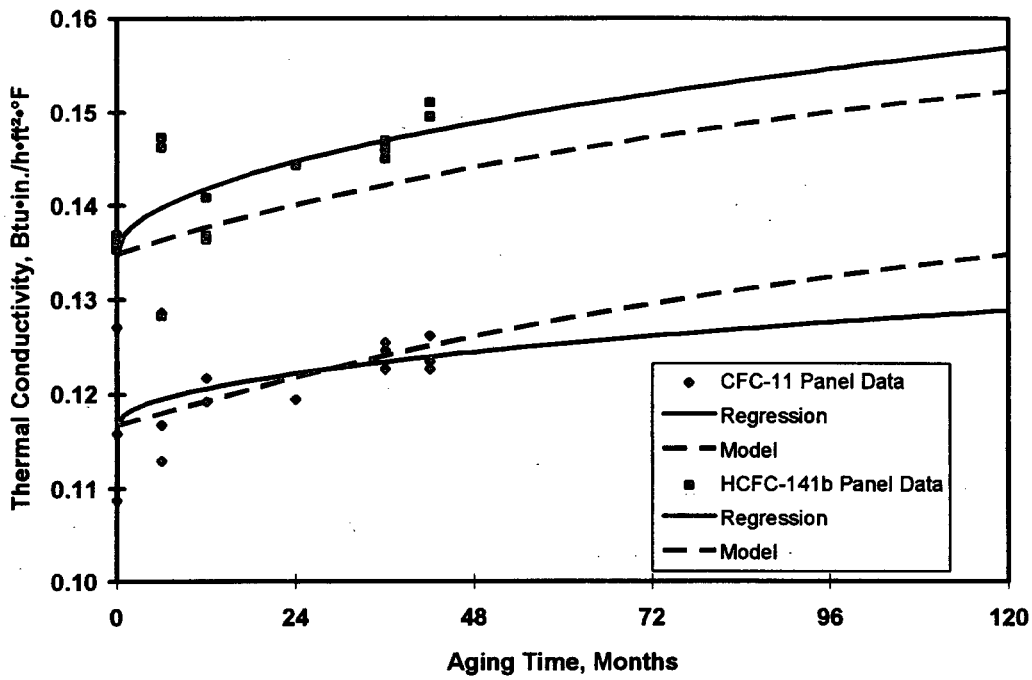

Figure 5. Comparison of Predicted and Measured Thermal Conductivities of Foams from Composite Test Panels

refrigerator application and will help to reduce the uncertainty in applying data obtained on test panels to the insulation in operating refrigerators. The effect of temperature on aging characteristics is expected to be complex. It is expected that the rate of diffusion of gases through the foam and permeation of gases through the liners will vary with aging temperature. Also, the blowing gases have boiling points that range from -15°F (for HFC-134a) to 121°F (for cyclopentane), and thus the liquid-vapor equilibrium will have an effect on aging characteristics.

Another factor that will be studied is the effect of different plastic materials that are used for refrigerator linings. In addition to the ABS plastic that has been used for the earlier studies, test panels will be fabricated using high-impact polystyrene (HIPS). Since gases permeate through HIPS faster than through ABS, aging of the foam insulation should occur faster with HIPS linings.[10] The plastic sheets will be 0.040 inches thick; this is considered to be a more typical thickness for use in refrigerators than the 0.12 inch thick plastic sheets that were used in the earlier study. For this study, both sides of the panels will have plastic sheets. This will allow gases to permeate through both sides of the panel and will provide an acceleration of the aging over that which would occur with steel on one side. It is expected that the effect of a steel boundary can be accounted for by the use of mathematical models.

In addition to the above factors, the test panels will be made by four foam suppliers, thus providing some information on variability of aging characteristics with foam formulations.

It is planned to perform thermal measurements on the panels at about six month intervals over a long period of time to track their aging characteristics. In addition to tests on full thickness panels, thin-slice core foam specimens will be prepared and measurements will be made on them over at least a 180 day period. Measurements on both the panels and core foam specimens will be performed at mean temperatures of 45°F and 75°F. Auxiliary measurements are planned for initial cell gas compositions, gas permeances of the plastic liner materials, and coefficients of diffusion of gases through the foams. Finally, the data obtained in this study will be compared with the predictions of mathematical aging models. These comparisons will be useful in validating the models and/or in providing information for further improvements of the models.

SUMMARY AND CONCLUSIONS

Thermal conductivity measurements have been made over a 3-1/2 year period on polyurethane foam insulation contained in composite test panels that simulate walls and doors of refrigerators. The test panels were blown with three blowing agents: CFC-11, HCFC-141b, and a HCFC-142b/22 blend, and were aged at 90°F. Thermal conductivity measurements were also made on specimens of the core foam taken from the panels. The data show that encapsulation of the foam insulation between solid steel and plastic liner boundaries greatly slows down the aging of the foam. For example, after 3-1/2 years of aging, the thermal conductivity of the CFC-11 blown foam in the test panels had increased by about 6 percent, while the thermal conductivity of unencapsulated core foam would have increased about 53 percent. Regression techniques have been used to extrapolate the thermal conductivity out to 10 years. Confidence intervals from these regressions suggest that at the end of 10 years of aging at 90°F, the thermal conductivity of the foam in the panels will increase by 3 to 18, 10 to 23, and 3 to 8 percent for CFC-11, HCFC-141b, and HCFC-142b/22 blowing agents, respectively. A mathematical model was constructed for the diffusion of air and blowing agents through the foam and for the permeation of these gases through the solid boundaries. Thermal conductivities predicted by the model are within a few percent of the extrapolated regression curves, lending some credence to the extrapolations.

A study of the aging characteristics of polyurethane foam insulation blown with new alternative blowing agents has started. This study includes foams blown with HCFC-141b, HFC-134a, HFC-245fa, and cyclopentane. This study will examine the influence of aging temperatures from -10°F to 90°F. Solid boundaries on test panels will be 0.040 inch thick ABS or HIPS plastics. One goal of this study will be to validate and/or improve mathematical models for aging of foam insulation contained within panels that simulate the construction of refrigerator walls and doors.

ACKNOWLEDGMENTS

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WATER SOLUTION OF POTASSIUM ACETATE IS AN OZONE-FRIENDLY, NON-TOXIC AND NON-CORROSIVE FIRE EXTINGUISHING AGENT

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Abstract: Long before a problem of Halon substitution arose, water fire extinguishers had been used onboard aircraft where each gram of equipment costs much. Nowadays owing to the tasks outlined by the Montreal Protocol and subsequent meetings, the urgency of developing an effective and safe fire extinguishing agent is absolutely clear.
The USSR-produced aircraft were equipped with portable fire extinguishers containing water-ethylene glycol agent (WEGA) to extinguish smoldering fires. The WEGA drawbacks were revealed in the process of its operation: corrosivity which resulted in fire extinguishers failure and limited service life. Moreover, an acute problem of used agent recovery was brought up since the agent contains a toxic component - ethylene glycol.

Analysis of technical materials, scientific literature and patent study showed a possibility to develop a water fire extinguishing solution with a low freezing point which is non-corrosive, non-toxic, affordable and has low production cost. Using both the gravimetric method and volumetric method, there were measured the corrosion rates for aluminum alloy, stainless steel (fire extinguisher main materials) and tin-lead solder at 70° C including fluid corrosion, corrosion along the waterline and contact corrosion in several salt solutions.

On the basis of the investigation results, there was selected a solution of potassium acetate with passivating additives. This solution refers to least dangerous group 4 which includes low-toxic substances as per ГОСТ USSR 12.1.007, whereas WEGA refers to group 3 of toxic substances. This solution was tested for physical and chemical properties, corrosivity and fire extinguishing capacity. The freezing point of 43% (mass $KOOCCH_3$ solution in distilled water with corrosion inhibitor additives is - 40°. The solution pH, density and viscosity for entire range of operation temperatures were defined. Fire extinguishers charged with solution were tested in the course of the following standard fires developed by "RD&PE Zvezda" JSC: liquid fuel fires, non-metal material fires and smoldering fires. Fire extinguishers' performances and ratings for Class B fire extinguishing were defined in comparison with nominal charges. Intensive thermal cyclic testing of charged fire extinguishers were performed. The testing made it possible to calculate the minimum warranty service life for fire extinguishers using the data on corrosion process activation energy and equivalent test and operations temperatures. The test results showed that compared with WEGA, the new agent:

- has lower corrosivity
- has lower toxicity
- contributes to improvement of ecological situation
- increases fire extinguisher service life
- has high fire extinguishing capacity (compared with that of Halon 1211)
- is cheaper.

This water solution has good application prospects both for fire extinguishers and for fire extinguishing systems of a "water mist" type.

INTRODUCTION

Among great variety of fire extinguishing agents, water is still beyond competition. Affordability, ecology friendliness, high heat capacity and non-toxicity are its indisputable advantages. To prevent water freezing, it is necessary to dissolve alcohols and salts in it. The most widely used are

water solutions of ethylene glycol (e.g. the Graviner fire extinguishers). In the 70-s, the USSR-produced aircraft were equipped with the Zvezda developed portable fire extinguishers of 1, 1.5, 2, 4 and 6 liter capacity which were charged with Halon 12B1 as well as with the 37% water-ethylene glycol agent (WEGA). The WEGA corrosivity relative to the siphon tubes made of the Д-16 aluminum alloy was revealed in the process of operation. These tubes failed in 1.5-2 years, therefore they started to produce the tubes of the 12X18H10T stainless steel. Later there came information about corrosion of fire extinguisher bottles made of the AMг-3 aluminum alloy. There were cases of corrosion through the fire extinguisher walls along the waterline and blow-holes in the bottle bottoms. The attempts to decrease corrosivity led to the test program for the "Arctica" anti-icing liquid which had been used in aviation. Besides water and ethylene glycol, Arctica includes 0.3% of Na_2HPO_4 as a corrosion inhibitor additive and 0.13% of surfactant admixture. During the test program, the question of ethylene glycol mixture toxicity was raised. When ethylene glycol gets into human organism, it acts as vessel and anti-plasmatic poison. This fact sets up problems both during agent utilization and recovery or regeneration. Moreover, ethylene glycol is flammable; it decreases fire extinguishing capacity of water. The necessity to give up WEGA have led to the search for non-toxic water solution with low freezing point, low corrosivity and higher fire extinguishing capacity than those of WEGA.

Analysis of technical and scientific literature and the patent study revealed the great scope of activities with water solutions of various salts and their mixtures. These fire extinguishing mixtures, side by side with advantages, had some of the following drawbacks: high corrosivity, toxicity, insufficiently low freezing point, complexity and unaffordability of the components. The experience gained made it possible to narrow the searched area by excluding corrosive halogenides of metals (Ca, Mg and others) [1]. Much attention was paid to potassium salts owing to information [2] that water fire extinguishing capacity improves when potassium carbonate or bicarbonate are added to water. This is associated with release (during evaporation) of free salts which, in fine dispersed state, actively inhibit fire development processes . The important role of viscosity in improving water fire extinguishing capacity by reducing its spreading capability, was investigated in paper [3]: increase of water viscosity up to 10-15 cP reduces fire extinguishing time by 5 times.

In some patents [4], potassium acetate was used as an improving and safe additive as well as the main agent [5] furthered careful study of potassium acetate solutions with various additives. The facts that 1) a composition [5] consisting of 300-600 g/l of potassium acetate, 2% (mass) of a wetting agent and 100 g/l potassium pyrophosphate featured high corrosivity regarding aluminum allows, and 2) according to the test data [6], 60% solution of potassium acetate demonstrated high fire extinguishing capacity at 5, 22 and 77° C, but froze at -18° C, indicate great importance of selecting concentrations for main substance and additives, and additive-to-additive relations.

A new fire extinguishing agent [8] was developed after a rather complex and long research [7]. It is 43% (mass) $KOOCCH_3$ solution in distilled water with addition of $Na_2SiO_3 \cdot 9H_2O$ (0.1% mass) and $Na_2B_4O_7 \cdot 10H_2O$ (0.3% mass) as corrosion inhibitor additives. The process of solution preparation is sequential dissolving of the components in distilled water by stirring.

PHYSICAL AND CHEMICAL PROPERTIES OF WATER SOLUTION OF POTASSIUM ACETATE (WSPA)

The solution density was measured with a general purpose hydrometer. The liquid temperature was preliminary controlled with accuracy of 0.5^{o}C. The results in comparison with WEGA are given in Table 1.

Table 1. Agent density (kg/l) depending on the temperature

Temp., ° C	- 30	- 20	- 10	0	10	20	30	40	60
WSPA	1.25	1.245	1.24	1.234	1.229	1.224	1.217	1.212	1.202
WEGA	freezes	1.07	1.063	1.057	1.051	1.044	1.039	1.032	1.020

The freezing point was defined with a Bauman-Fromm instrument. The temperature when the solid phase appeared during cooling and disappeared during heating, was registered with a thermometer having the accuracy of ±0.5° C. The WSPA freezing point was -40° C that is significantly lower than that of WEGA (-20...25° C).

The WSPA boiling point was 112±2° C (under atmospheric pressure).

The viscosity was defined with the ВПЖ-2 capillary viscometer. The results in comparison with WEGA are given in Table 2.

Table 2. Agent viscosity (cP) depending on the temperature

Temp., ° C	- 30	- 20	- 10	- 5	0	3	10	20	30	40	50
WSPA	30	15.3	9.4	8.3	-	6.1	4.8	3.45	2.66	2.15	1.48
WEGA	-	-	8.2	-	5.2	-	-	2.57	1.87	1.49	1.01

The solution pH was defined by potentiometric method using glass and Cl-Ag electrodes. The results showed that WSPA is neutral, pH is 8±0.5.

FIRE EXTINGUISHING PROPERTIES OF WSPA

The efficiency of the fire extinguishing agent was defined as per Class A and Class B fire extinguishment. According to the adopted classification, Class A fires are fires of solid mainly organic substances which can be accompanied with smoldering, and Class B fires are fires of flammable liquids. The reproducible model fires have been developed for each class of fires. Either positive or negative result is to be registered upon test completion. In case of successful fire extinguishment, we registered time and agent mass used for extinguishment. We also registered temperature and existence of wind. We used the OP1-1 (1 liter) and OP1-2 (2 liter) portable aircraft fire extinguishers.

The adopted international standard of Class A fires is a 0.5 x 0.5 x 0.8 m (width x height x length) lumber pile of bars with 40 x 40 mm cross-section [9]. Due to the specific character of the airplane structure and interior fires, this model was unacceptable for our test program because it was bulky and made of only one material. Therefore, there was developed a test facility [10]. It is a 4-sheet package fixed vertically on the stand (two sheets of two materials alternating with each other and having different rate of burning). Two 3 mm sheets of the P-29 rubber and two 18 mm sheets of the ПС-4 foam plastic form a 42 mm thick, 450 mm high and 290 mm wide package. To fire this package, there is made a ∅ 30 mm hole through the package, 100 mm above its lower edge, and a wick soaked in gasoline is put into the hole to provide for simultaneous inflammation of all package layers. The fire extinguisher is actuated in a minute after setting the fire when the flame is about 1 m heigh and the package is half-burnt. Since rubber and foam plastic feature different rates of burning, the model is characterized by concealed and difficult for direct extinguishment fire centers. The burning package has access for fire extinguishing from any side.

The results of Class A fire extinguishing with various agents are given in Table 3. The data show that in Class A fire extinguishment the WSPA efficiency at room temperature is not lower than that of WEGA, and it is significantly higher at cooling (cooling is much lower).

We also run the tests on extinguishment of smoldering fires. A rectangular metal structure (450 x 290 x 42 mm) with wire mesh (36 x 36 mm) walls was filled with 250-300 g of cotton and cleaning cloth. To set a smoldering fire, the material was burnt to have a stable open fire, then there was the flame-out, and the smoldering fire developed during 30-40 minutes till it covered half of the package. Total extinguisment of all smoldering points was obtained only by wetting of all smoldering material. On the results of testing with the OP1-2 fire extinguisher, it was shown that the WSPA capacity in extinguishing of the smoldering fire is not worse than that of WEGA.

According to the international standard ISO, Class B model fire is the burning of liquid fuel in a round pan. The fire extinguisher rating was defined by the maximum dimension of the pan where it can extinguish fire. Unlike the adopted set of 11 various pans [9, 11] which are filled with 31.4 mm-thick layer of fuel (fuel quantity in liters defines a fire index), the Zvezda test facility was modified from the point of operator safety and comfort, fuel saving and ecology improvement [12].

Table 3. Class A fire extinguisment

Test #	Agent	Type of fire ext-er	Charged mass, kg	Agent temp.,°C	Distance from fire center, m	Time of exting-t, s	Mass used, kg
1.	WSPA	OP1-1	0.92	20	1.0	7	0.7
2.	WSPA	OP1-1	0.92	15	1.5	8	0.8
3.	WSPA	OP1-1	0.92	-30	1.0	8	0.85
4.	WSPA	OP1-2	1.84	20	2.0	10	1.05
5.	WSPA	OP1-2	1.84	-30	2.0	12	1.1
6.	WSPA	OP1-2	1.84	-30	2.0	15	1.35
7.	WEGA	OP1-1	0.84	15	1.0	8	0.8
8.	WEGA	OP1-2	1.68	15	1.5	11	1.0
9.	WEGA	OP1-2	1.68	15	2.0	15	1.35
10.	WEGA	OP1-2	1.68	-20	2.0	19	1.65
11.	Halon 1211	OP1-1	1.37	20	1.5	4	0.4
12.	Halon 1211	OP1-1	1.37	-60	1.5	4	0.45

This facility is a 3.0 x 3.0 x 0.2 m pan which is filled with at least 30 mm-thick layer of water. Then round shells of calculated diameter are sequentially put into the pan. The shells are filled with the T-1 aviation fuel in a quantity to form a fuel layer of 3.1 mm-thick and time of its burn-out not more than 2.5 min. The time from ignition to start of extinguisment was 1 min., and all surface inside the shell was covered with fire in 15-20 seconds. In case of the negative result that is when the fire was not extinguished, the fuel would totally burn out in 1.5 min whereas according to method [9, 11], the fuel would burn 20-25 min more or would be extinguished with more efficient fire extinguisher releasing additional quantity of the agents. Dimensions of the shells and fire areas, fuel quantity and fire index are given in Table 4.

Table 4. Parameters of the Class B model fire test facility

#	Shell diameter, m	Fire area, m²	Fuel q-ty, l	Fire index
1	0.2	0.032	0.1	1B
2	0.28	0.065	0.2	2B
3	0.34	0.094	0.3	3B
4	0.44	0.16	0.5	5B
5	0.56	0.24	0.8	8B
6	0.72	0.41	1.3	13B

#	Shell diameter, m	Fire area, m²	Fuel q-ty, l	Fire index
7	0.91	0.65	2.1	21B
8	1.20	1.10	3.4	34B
9	1.34	1.41	4.5	45B
10	1.50	1.76	5.5	55B
11	1.70	2.27	7.0	70B
12	1.90	2.81	8.9	89B
13	2.12	3.54	11.3	113B
14	2.40	4.52	14.4	144B
15	2.71	5.75	18.3	183B

Note: the designers of fire index series [9] took a series of Fibonacci numbers where the next number is the sum of two previous numbers.

The test results are given in Table 5. As Table 5 shows, the WSPA fire extinguishing capacity is higher than that of WEGA. Using the OP1-1 fire extinguisher, the fire of 8B index was extinguished with WSPA in 5.5 s three times in succession, whereas with WEGA, it was extinguished only once of three times in 11 s. Using the OP1-2 fire extinguisher, the fire of 13B index was extinguished with WSPA in 2.5 s two times, and using WEGA - in 18 s. The data shown in Table 5 refer to the temperature of agents and environment in the range of 20-26° C. The results for low temperatures (omitted here) show even much better fire extinguishing capability of WSPA compared to that of WEGA.

Table 5. Class B fire extinguishment

#	Agent	Type of FE	Charge mass, kg	FE pressure, kgf/cm²	Fire index	Fire area, m²	Result	Time of ext-t, s	Mass spent, kg	Wind
1	WSPA	OP1-1	0.92	10	8B	0.24	+	4	0.46	gentle
2	WSPA	OP1-1	0.92	10	8B	0.24	+	4.5	0.54	gentle
3	WSPA	OP1-1	0.92	10	8B	0.24	+	8.0	0.80	gentle
4	WSPA	OP1-1	0.92	10	13B	0.41	-	-	0.90	gentle
5	WSPA	OP1-1	0.92	10	13B	0.41	+	9.0	0.84	gentle
6	WSPA	OP1-1	0.92	10	13B	0.41	-	-	0.90	gentle
7	WSPA	OP1-2	1.84	10	13B	0.41	-	-	1.80	gusty
8	WSPA	OP1-2	1.84	12	13B	0.41	+	2.0	0.23	gusty
9	WSPA	OP1-2	1.84	12	13B	0.41	+	3.0	0.32	gusty
10	WSPA	OP1-2	1.84	12	21B	0.65	-	-	1.80	gusty
11	WEGA	OP1-1	0.84	10	8B	0.24	-	-	0.80	gentle
12	WEGA	OP1-1	0.84	10	8B	0.24	+	11.0	0.80	gentle
13	WEGA	OP1-1	0.84	10	8B	0.24	-	-	0.80	gusty
14	WEGA	OP1-1	0.84	10	13B	0.41	-	-	0.80	gusty
15	WEGA	OP1-1	0.84	10	13B	0.41	-	-	0.80	gusty
16	WEGA	OP1-2	1.68	12	13B	0.41	+	18	1.52	gusty
17	WEGA	OP1-2	1.68	12	13B	0.41	+	18	1.49	gusty
18	Halon 12B1	OP1-1	1.37	10	45B	1.41	+	8	0.81	strong
19	Halon 12B1	OP1-2	2.74	10	55B	1.76	+	10	1.10	gusty

WSPA CORROSIVE PROPERTIES

In preliminary testing with potassium carbonate solution (one of the agents researched), it was established that the rate of Амг-3 alloy corrosion along the waterline many times exceeded the corrosion rate of wholly immersed sample. Therefore, all the researches were run with partial immersion of the samples into the researched solution. The measurements were done by the gravimetric method, i.e. by changes of the sample's mass in a certain period of time; the corrosion rate was expressed in $g/m^2 \cdot day$. In some cases, the aluminum alloy corrosion was studied by the volumetric method i.e. by measuring the volume of hydrogen released during aluminum dissolving, and then the volume was recalculated into the mass of corroded metal.

Table 6 shows relationship between corrosion rate of the metal alloys, which were used to manufacture the bottle (Амг-3) and siphon tubes (Д-16 and 12X18H10T), and duration of test in WSPA and WEGA along the waterline.

Table 6. Rate of alloys corrosion in solutions at 70° C

Alloy	Corrosion rate K ($g/m^2 \cdot day$)				
	WSPA (90 h)	WSPA (150 h)	WSPA (270 h)	WEGA (100 h)	WEGA (200 h)
AMг-3	0	0	0	0	+0.014
Д-16	0	+0.0096	+0.005	+0.07	+0.062
12X18H10T	0	-0.0096	-0.005	-0.028	-0.024

Symbol "+" in Table 6 means gain in the sample mass and symbol "-" means loss of the sample mass. The corrosion rate was calculated on the basis of sample mass changes and assumption that all samples corrode uniformly. As Table 6 shows, the corrosion rate in WSPA along the waterline is many times lower than that in WEGA. Since in real operation conditions all metals in the fire extinguisher are in electrochemical contact, we measured metal corrosion during their contact. Table 7 gives values of contact corrosion rate at 70° C in WSPA and WEGA.

The results show that the emf of the AMг-3/steel pair in both solutions is higher than that of the AMг-3/Д-16 pair, which can be explained by the difference of aluminum and steel electronic potentials. The emf reduces with the time but in a month the AMг-3/steel pair emf in WSPA was 4 times lower than that in WEGA, and the AMг-3/Д-16 pair emf in WSPA was 20 times lower than that in WEGA. These facts corroborate the low corrosivity of WSPA in comparison with WEGA.

Table 7. Rate of contact corrosion for metals at 70° C depending on the test duration in WSPA and WEGA

Contacting metals	Contact corrosion rate, $g/m^2 \cdot day$ (mm/year)			
	Test duration in WSPA, h			
	150	250	500	
Амг-3 12X18H10T	0.0093 (0.00124) 0	0.0110 (0.00147) 0.0013 (0.00006)	0.0083 (0.0011) 0.0019 (0.00009)	
Амг-3 Д-16	0 0.0021 (0.00028)	0.0083 (0.0011) 0.0026 (0.00035)	0.0056 (0.00075) 0.0025 (0.00033)	
	Test duration in WEGA, h			
	100	210	440	675
Амг-3 12X18H10T	0.313 (0.042) 0.038 (0.0018)	0.22 (0.0029) 0.018 (0.00084)	0.22 (0.029) 0.011 (0.00051)	0.19 (0.025) 0.0085 (0.0004)
Амг-3 Д-16	0.084 (0.011) 0.029 (0.004)	0.079(0.01) -	0.071 (0.009) 0.0022 (0.0003)	0.062 (0.0082) 0.0028(0.00037)

The electrochemical mechanism of corrosion is explained by the fact that the metals in the fire extinguishing solution are in the state of electrical contact and forms a galvanic system. Therefore, it is very important to measure an electromotive force (emf) between metals in solutions. The emf was measured with a high-ohm microvoltmeter under conditions of natural aeration and room temperature. The metal samples were degreased with acetone and fixed in the solution. After measurement of the emf between the samples, they were connected with copper wire. In certain time periods, the samples were disconnected, and the potential was measured. The results obtained are given in Table 8.

Table 8. Measurement of the emf between samples in the solutions

Water solution	Metal pair	Potential, mV						
		Test duration, day						
		0	2	4	16	25	28	30
WEGA	AMг-3/12X18H10T	980	500	440	370	330	270	260
	AMг-3/Д-16	230	180	136	105	119	112	110
WSPA	AMг-3/12X18H10T	870	340	250	70	62	65	65
	AMг-3/Д-16	330	160	99	6	6	6	3

SERVICE LIFE OF FIRE EXTINGUISHERS CHARGED WITH WSPA

The minimum service life was defined with the method of intensive thermal cyclic testing [13] by heating the fire extinguishers to the temperature beyond the operation one. For this purpose, we tested 15 portable fire extinguishers of the OP type. Five fire extinguishers were charged with WSPA, water solution of potassium acetate with additives, another five - with the 37% water-ethylene glycol agent (WEGA), and five - with the "Arctica" anti-icing liquid (ARCT). The bottles were filled with the liquids up to 0.4 of the bottle capacity and pressurized with nitrogen up to 10 kgf/cm^2. The charged bottles were put into a thermal chamber where the temperature changed according to the following mode:

- *day cycle*: 14 h at 80° C, 9 h linear decrease of temperature down to 50° C, 1 h linear increase of temperature up to 80° C;
- *week cycle*: five day cycles, 9 h linear decrease of temperature from 50° C to 20°C, 39 h at 20°C.

The first random inspection of 6 fire extinguishers was carried out in 1.5 month. By that time, the fire extinguishers stayed at 80° C for 316 h, at 65° C - 300 h and at 20° C - 500 h. All fire extinguishers kept the charged pressure. After nitrogen exhaust, the liquids were transferred into glass vessels. During inspection of the inner surfaces, bottoms and siphon tubes, it was found out that:

- fire extinguishers OP1-2 #0231176 and OP2-4 #0451005 charged with ARCT have ∅3-4 mm dark stains on the bottoms;

- bottoms of fire extinguishers OP1-2 #0262161 and OP2-4 #0451007 charged with WEGA have pitting corrosion centers of ∅1.5-2 mm with ∅6-8 mm halo around them; OP1-2 has 9 pitting centers and OP2-4 has 4 ones;

- fire extinguishers OP1-2 #0671560 and OP2-4 #0451000 charged with WSPA have no corrosion.

After inspection, the fire extinguishers were charged with the same liquids and pressurized with nitrogen up to 10 kgf/cm^2. Further the fire extinguishers were also inspected, and if there were mass decreases, bottle painting destruction due to walls swelling, and some other abnormalities, the fire extinguishers were withdrawn from the test prior to the test cycle completion:

- OP1-2 #0231176 (ARCT) - in 5 months, due to pressure decrease down to 6.5 kgf/cm^2 (0.2 kg mass loss), paint blistering at the waterline level, leak through the wall under the pressure of 20 kgf/cm^2;
- OP1-2 #1055047 (ARCT) - in 5 months, loss of pressure (mass decrease by 0.63 kg), a wall-through hole a little bit above the bottom, black stain around the hole inside the bottle;
- OP1-2 #0262161 (WEGA) - in 5 months, loss of pressure and liquid through the blow-hole in the bottom, there is much corrosion on the walls;
- OP1-2 #0571385 (WSPA) - in 6 months, loss of pressure (due to a diaphragm defect), no corrosion anywhere;
- OP1-1.5 #0280523 (ARCT) - in a year, big swelling of the wall with paint damage, mass and pressure are the same, much pitting on the walls and bottom;
- OP1-1.5 #0280510 (ARCT) - in a year, the same causes as in the previous case.

The other 9 fire extinguishers were tested during 20.5 months, then they were checked, discharged and inspected:

- OP2-6 #0670563 (WEGA) - pitting on the walls is clearly seen;
- OP2-6 #0152000 WSPA) - the walls and siphon tube are clean, no corrosion, there is a boundary between phases;
- OP2-6 #1041100 (WEGA) - corrosion pits on the walls are clearly seen, pitting on the siphon tube is seen under the white deposit;
- OP2-4 #0451007 (WEGA) - there are the big white deposit on the siphon tube, the pronounced boundary between the phases, corrosion, much pitting on the bottom;
- OP2-4 #0451005 (ARCT) - there are much corrosion on the bottom, brown and black stains, pitting on the walls;
- OP2-4 #0451000 (WSPA) - the walls and siphon tube are clean, no corrosion, the boundary between phases is seen;
- OP1-2 #0671560 (WSPA) - the walls and siphon tube are clean, no corrosion, the boundary between phases is not seen;
- OP1-1.5 #0002106 (WSPA) - the walls and siphon tube are clean, no corrosion, the boundary between phases is seen;
- OP1-1.5 #0772110 (WEGA) - there is the white deposit on the siphon tube, corrosion pits are seen under the deposit, pitting on the walls is pronounced.

The transferred liquids had the following appearance: ARCT - white flakes, yellowish color; WEGA - white with little turbidity; WSPA - clear.

Five fire extinguishers of the six OP1-2 and OP1-1.5 type fire extinguishers (with 2 mm thick walls) which were charged with WEGA and ARCT, were withdrawn from testing prior to its completion (3 in half a year, 2 in a year), and only one fire extinguisher went through the testing but it had much corrosion. All fire extinguishers of the OP2-4 and OP2-6 type (with 3 mm thick walls) charged with WEGA and ARCT kept pressure to the end of testing but had much pitting on the bottoms, walls and siphon tubes. All fire extinguishers charged with WSPA were clean, no corrosion.

The designed service life of fire extinguishers charged with the agents τ_{serv} relates [13] to design test time τ_{test} by the formula:

$$\tau_{serv} = \tau_{test} \cdot e^{\frac{E}{R}\left(\frac{1}{T_{serv}} - \frac{1}{T_{test}}\right)} , \qquad (1)$$

where E - corrosion activation energy, kCal/mol

R - universal gas constant, 1.99 Cal/mol·deg;

T_{serv} - equivalent service temperature

T_{test} - equivalent test temperature

Activation energy E was defined [14] by the formula (2):

$$E = -R\frac{\Delta \ln K}{\Delta(1/T)} , \qquad (2)$$

where ΔlnK - difference of the logarithm of corrosion rate in the range of Δ(1/T).

To calculate E, we measured the average rate of contact corrosion for the Амг-3 alloy (g/m²·day) in WSPA at 20, 50 and 75° C: K_{20}=0.008; K_{50}=0.022 and K_{75}=0.042.

These test data made it possible to establish the linear dependence of lnK from Δ(1/T) (-4.83, -3.82, -3.17 at 0.00341, 0.00309 and 0.00287, correspondingly). Average AMг-3 corrosion activation energy in WSPA is 6.2 kCal/mol. With the known cycle of changes, the equivalent temperatures were calculated by formula:

$$T_{eq} = -\frac{E}{R}\left[\ln\left(\frac{1}{\tau_0}\Sigma\, \tau_i \cdot e^{-\frac{E}{RT_i}}\right)\right]^{-1} , \qquad (3)$$

where τ_i - time of stay at the temperature of T_i

τ_o - sum of all τ_i

To calculate the equivalent service temperature, we assume that the fire extinguisher stays during 10% of the whole service life at 40° C, the average of the maximum operation temperature (60° C) and room temperature; 10% - at 0° C, the average of the minimum service temperature (-20° C) and room temperature; 80% - at 20° C. To calculate the equivalent test temperature, we assume that the total test time τ_o=14930 h This total consists of: 5700 h at 80° C, 4200 h at 65° C, 5030 h at 20° C with the total number of heating/cooling cycles equal to 420. With substitution of these values in the formula (3), we get $T_{eq(test)}$=62° C (335K) and $T_{eq(serv)}$=21° C (294K).

With substitution of the calculated values into the formula (1), we get the minimum service life of the OP type fire extinguishers at the equivalent service temperature of 21° C which is equal to 6.2 year (no corrosion traces). This was defined in the 20.5 month testing at the equivalent temperature of 62° C for the corrosion process with the activation energy of 6.2 kCal/mol.

Similar calculations on the test results of the OP type fire extinguisher charged with water-ethylene glycol mixtures showed that their service life is 2-4 years.

CONCLUSION

There was developed and tested a new fire extinguishing agent, water solution of potassium acetate with sodium silicate and sodium tetraborate additives. In comparison with water-ethylene glycol agent, the new agent is safe, has lower corrosivity and better fire extinguishing capacity, expands operation temperature range and contributes to improvement of ecological situation. According to the results of the research run by the specialists of the Moscow Institute of Hygiene and Sanitary named after F.F. Erisman, the new agent refers to least dangerous group 4 which includes low-toxic substances as per ГОСТ USSR 12.1.007, whereas WEGA refers to group 3 of toxic substances.

The new agent can be used both in the onboard aircraft fire extinguishers and fire extinguishers of other application, as well as in the fire extinguishing systems of a "water mist" type. The Kidde International Technical Note [15] presents technical requirements to low-freezing liquids. They are identical to those set and solved in this paper. Therefore, we believe that the new agent has good prospects. Moreover, acetate solutions with inhibitor additives can be used as ecology-friendly, glycol-free antifreezes for automobiles as well as for other purposes requiring heat and cool transfer.

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Fine Water Mist - Fire Control Using Local Application

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Introduction

The United States Coast Guard (USCG) is responsible for establishing fire safety standards for U.S. flag ships via 46 Code of Federal Regulations. The USCG is also active in establishing and enforcing rules for fire safety on vessels making international voyages through the International Maritime Organization (IMO). Both the USCG and the IMO have recognized that the phaseout of Halon 1301 due to its ozone depletion potential has created an urgent need for the development of alternative protection.

One of the alternatives for fire protection of shipboard machinery spaces is fine water mist. Total space protection using fine water spay is allowed under the IMO's Safety of Life at Sea (SOLAS) regulations. The requirements for total space protection are contained in the Maritime Safety Committee's (MSC) Circular 668 [1]. The MSC's Fire Protection (FP) subcommittee is scheduled to consider local application protection for high risk components at its 41st meeting (December 1997).

The local application protection being considered would be additional protection for specific high risk components, e.g., main engines, diesel generator sets, fuel strainers and purifiers. This would supplement the existing required total space protection, be it a gas, fine water spray or high expansion foam. The goal would be to provide protection at the source, in a quicker time frame, without functional loss of other items in the space, and to potentially aid in or eliminate the need for space evacuation.

The USCG as part of its regulatory authority, had a need to assess the benefits and feasibility of local protection as well as determine an effective method of evaluating potential systems. The tests hereafter described were conducted by the USCG Research and Development

Center (R&DC) at the request of U.S. Coast Guard Marine Safety and Environmental Protection (G-M) organization to address this need.

Objective

The testing conducted was designed to meet the following objectives:

1. Assess the feasibility of local application of fine water mist for component level protection.
2. Evaluate a range of fine water mist parameters, i.e.; large drops, small drops, high and low momentum mist, nozzle flow rate, and nozzle spacing over a variety of fire sizes and conditions.
3. Investigate key parameters that a test protocol should include to effectively evaluate candidate systems.

Nozzles Tested

Seven generic nozzles that produced a variety of mists were tested. These were off the shelf industrial spray nozzles selected for their spray pattern and characteristics, see Table 1. They represented the extremes of currently available water mist systems. One Underwriter's Laboratory (UL) listed National Fire Protection Association (NFPA) Chapter 15 (NFPA 15) [2] water spray nozzle was also tested for comparison purposes.

Table 1. Nozzle Characteristics

Nozzle Designation	Operating Pressure (bar)	k-factor (Lpm-bar$^{1/2}$)	Spray Angle	Spray Classification (NFPA 750)
UL/NFPA-15	7	16.85	Wide	Sprinkler
Generic 1	5	4.3	Narrow	Class 3
Generic 2	70	1.0	Narrow	Class 1-2
Generic 3	10	3.2	Wide	Class 3
Generic 4	70	0.9	Wide	Class 1-2
Generic 5	35	0.4	Narrow	Class 1-2
Generic 6	70	1.9	Wide	Class 1-2

The generic nozzles produced wide and narrow angle low pressure Class 3 and wide and narrow angle high pressure Class 1-2 sprays as defined by NFPA 750 [3]. The high pressure nozzles generated small droplets with a Dv_{90} of 100 to 400 microns. The low pressure nozzles generated larger droplets with a Dv_{90} of over 400 microns up to 535 microns. The UL listed NFPA 15 nozzle generated droplets with a Dv_{90} of up to 1200 microns.

Test Setup

The tests were conducted at the U.S. Coast Guard's Fire & Safety Test Detachment in Mobile, Alabama. This unique fire test facility allows actual fire tests to be conducted onboard ships. The tests were conducted onboard the test vessel STATE OF MAINE. The test compartment was 10 x 10 x 5 m for a total volume of 500 m^3 and meets the requirements of other IMO machinery space test protocol including MSC Circular 668 [1].

A series of spray fires and pan fires were run against a four (UL listed NFPA 15 nozzle in accordance with its listing) or nine nozzle arrays in three different configurations. The nozzles had either a 1 or 2 meter spacing and were typically evaluated 2 meters from the fire. Other distances (1 and 3 meters) where tried, but were found to be ineffective due to spray pattern deficiencies. The fires ranged in size from 1 MW up to 6 MW. The fuel was heptane or diesel.

The three test configurations consisted of horizontal nozzle arrays (Top and Low) located above the fire spraying vertically down, or a vertical nozzle array (Side) beside the fire spraying horizontally, as shown in Figure 1. While in practice, a local application system may completely surround the component, this one direction of spray was felt to be the most serve case. Two horizontal array locations were tested. The first was located just below the compartments overhead (Top) and the second was located 2 meters below the overhead (Low). This low configuration was established to reduce the effects of the nozzles entraining the vitiated fire products from the small ceiling layer that did form.

The test compartment was kept well ventilated by a forced supply air system and an open 6 m2 exhaust stack located in the top of the compartment. The supply blower was sized to produce approximately 20 air changes an hour.

The test compartment was instrumented to record compartment temperatures, pressure, heat flux, and gas concentrations. Probes at the fire location recorded fire temperatures and local oxygen concentrations. The water distribution system was instrumented to record system pressure at various locations throughout the network. Video cameras were used to monitor and record the tests.

Once the compartment ventilation conditions were set. The fires were ignited and allowed to burn for one minute. The fine water mist system was then actuated and allowed to run for 15 minutes or until the fire was extinguished. Fire extinguishment times and other instrument readings were recorded.

Results

Ninety-three tests of local application of fine water mist were conducted in this evaluation. Twenty-six tests were run with a vertical nozzle grid at the side location, see Table 2. Seventeen tests with the horizontal nozzle grid were run at the top location, see Table 3. Fifty tests were run with the lower horizontal nozzle grid in the low location, see Table 4. For the purposes of this paper, the analysis of the results will be presented in terms of extinguishment when the fires were extinguished or fire control when the fires were not extinguished.

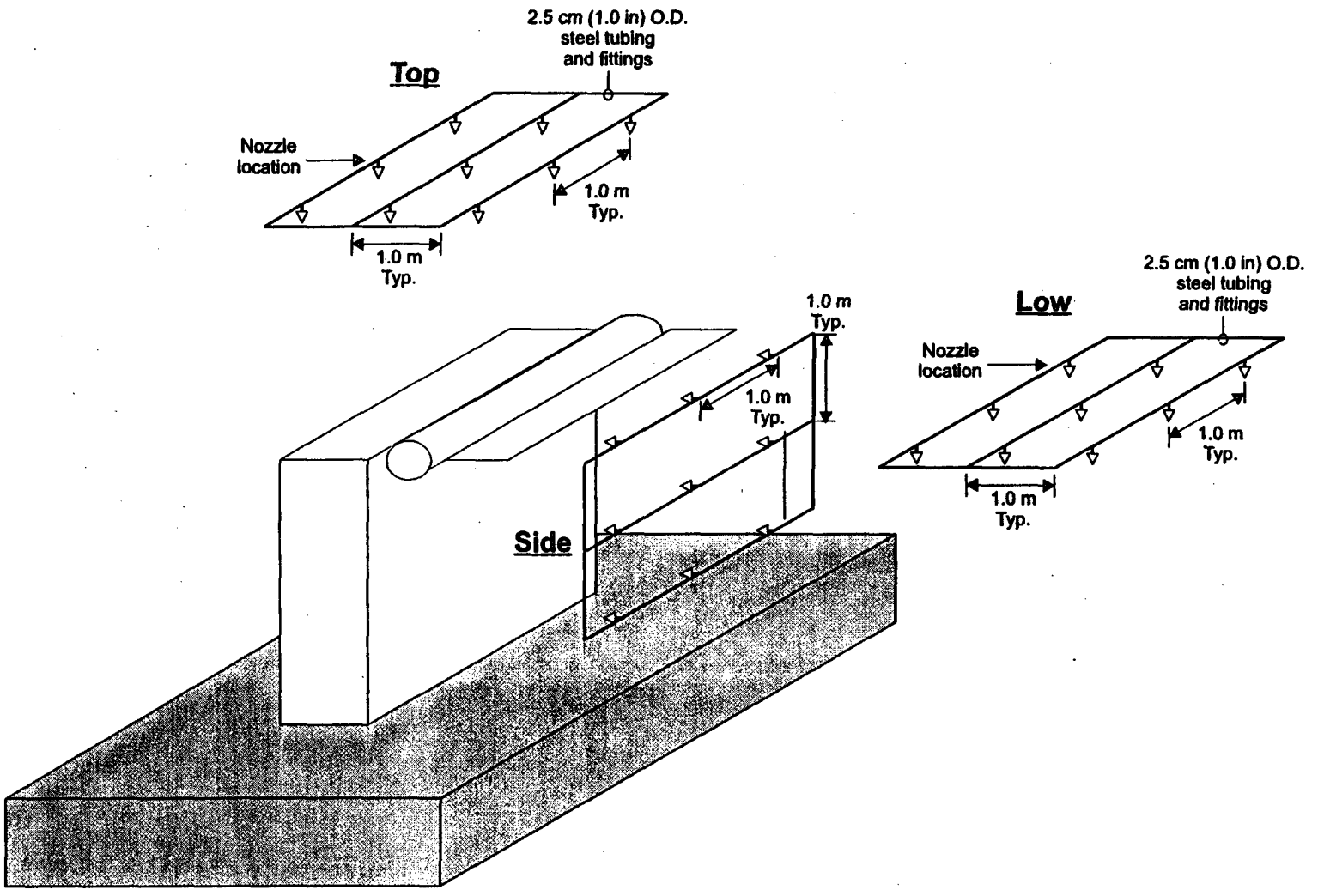

Figure 1 — Local application water mist systems

Table 2. Vertical Nozzle Grid - Side Location Results

Test No.	Nozzle Spray Direction	Grid Location	Nozzle	Pressure (bar)	Nozzle Dist. (m)	Nozzle Spacing (m)	Fire Size (MW)	Fire Type	Fire Location (Figure 5)	Exting. Time (min:sec)
1	Horizontal	Side	NFPA-15	7	2	2	1.0	Diesel Spray	Side	No
2	Horizontal	Side	NFPA-15	7	2	1	1.0	Diesel Spray	Side	No
3	Horizontal	Side	G-3	7	2	1	1.0	Diesel Spray	Side	No
4	Horizontal	Side	G-3	7	2	1	1.0	Diesel Pan	Side	2:30
5	Horizontal	Side	NFPA-15	7	2	2	1.0	Diesel Pan	Side	No
6	Horizontal	Side	G-1	7	2	1	1.0	Diesel Pan	Side	1:35
7	Horizontal	Side	G-4	70	2	1	1.0	Diesel Pan	Side	1:45
8	Horizontal	Side	G-2	70	2	1	1.0	Diesel Pan	Side	No
9	Horizontal	Side	G-2	35	2	1	1.0	Diesel Pan	Side	4:09
12	Horizontal	Side	G-2	35	2	1	1.0	Diesel Spray	Side	No
13	Horizontal	Side	G-2	35	2	1	1.0	Diesel Spray	Side	No
14	Horizontal	Side	G-2	35	2	1	6.0	Diesel Spray	Side	No
15	Horizontal	Side	G-4	70	2	1	6.0	Diesel Spray	Side	No
16	Horizontal	Side	G-4	70	2	1	1.0	Diesel Spray	Side	No
17	Horizontal	Side	G-1	7	2	1	1.0	Diesel Spray	Side	No
18	Horizontal	Side	G-1	7	2	1	6.0	Diesel Spray	Side	No
19	Horizontal	Side	G-3	7	2	1	6.0	Diesel Spray	Side	No
20	Horizontal	Side	G-3	7	2	1	1.0	Diesel Spray	Side	No
21	Horizontal	Side	NFPA-15	7	2	2	1.0	Diesel Spray	Side	No
22	Horizontal	Side	NFPA-15	7	2	2	6.0	Diesel Spray	Side	No
23	Horizontal	Side	G-4	70	2	1	6.0	Diesel Spray	Side	2:57
24	Horizontal	Side	G-4	70	2	1	1.0	Diesel Spray	Side	No
25	Horizontal	Side	G-2	35	2	1	6.0	Diesel Spray	Side	No
26	Horizontal	Side	G-2	35	2	1	3.0	Diesel Spray	Side	No
27	Horizontal	Side	G-3	7	2	1	3.0	Diesel Spray	Side	No
28	Horizontal	Side	G-3	7	2	1	6.0	Diesel Spray	Side	No

Table 3. Horizontal Nozzle Grid - Top Location Results

Test No.	Nozzle Spray Direction	Grid Location	Nozzle	Pressure (bar)	Nozzle Dist (m)	Nozzle Spacing (m)	Fire Size (MW)	Fire Type	Fire Location (Figure 5)	Exting. Time (min:sec)
29	Vertical	High	G-4	70	2	1	1.0	Diesel Spray	Top	0:11
30	Vertical	High	G-4	70	2	1	6.0	Diesel Spray	Top	0:09
31	Vertical	High	G-4	70	2	1	1.0	Diesel Pan	Top	0:05
32	Vertical	High	G-2	35	2	1	1.0	Diesel Pan	Top	0:55
33	Vertical	High	G-2	35	2	1	1.0	Diesel Spray	Top	0:53
34	Vertical	High	G-2	35	2	1	6.0	Diesel Spray	Top	0:21
35	Vertical	High	G-3	7	2	1	1.0	Diesel Spray	Top	0:32
36	Vertical	High	G-3	7	2	1	6.0	Diesel Spray	Top	0:11
37	Vertical	High	G-3	7	2	1	1.0	Diesel Pan	Top	0:09
38	Vertical	High	G-1	7	2	1	1.0	Diesel Pan	Top	0:40
39	Vertical	High	G-1	7	2	1	1.0	Diesel Spray	Top	3:05
40	Vertical	High	G-1	7	2	1	6.0	Diesel Spray	Top	0:22
41	Vertical	High	NFPA-15	7	2	2	1.0	Diesel Spray	Top	No
42	Vertical	High	NFPA-15	7	2	2	6.0	Diesel Spray	Top	No
43	Vertical	High	NFPA-15	7	2	2	1.0	Diesel Pan	Top	No
75	Vertical	High	G-3	7	3	1	1.0	Diesel Spray	Side	No
76	Vertical	High	G-4	70	3	1	1.0	Diesel Spray	Side	No

Table 4. Horizontal Nozzle Grid - Low Location Results

Test No.	Nozzle Spray Direction	Grid Location	Nozzle	Pressure (bar)	Nozzle Dist (m)	Nozzle Spacing (m)	Fire Size (MW)	Fire Type	Fire Location (Figure 5)	Exting. Time (min:sec)
73	Vertical	Low	G-4	70	2	1	1.0	Diesel Spray	Low	4:24
74	Vertical	Low	G-3	7	2	1	1.0	Diesel Spray	Low	No
111	Vertical	Low	G-4	70	2	1	6.0	Diesel Spray	Low	0:41
112	Vertical	Low	G-4	70	2	1	3.0	Diesel Spray	Low	0:59
113	Vertical	Low	G-4	70	2	1	1.0	Diesel Spray	Low	3:01
114	Vertical	Low	G-4	70	2	1	6.0	Heptane Spray	Low	1:30
115	Vertical	Low	G-4	70	2	1	3.0	Heptane Spray	Low	1:25
116	Vertical	Low	G-4	70	2	1	1.0	Heptane Spray	Low	3:03
117	Vertical	Low	G-4	70	2	1	1.0	Diesel Pan	Low	0:09
118	Vertical	Low	G-4	70	2	1	1.5	Heptane Pan	Low	0:11
119	Vertical	Low	G-2	35	2	1	1.5	Heptane Pan	Low	0:07
120	Vertical	Low	G-2	35	2	1	1.0	Diesel Pan	Low	0:10
121	Vertical	Low	G-2	35	2	1	6.0	Heptane Spray	Low	0:31
122	Vertical	Low	G-2	35	2	1	3.0	Heptane Spray	Low	0:57
123	Vertical	Low	G-2	35	2	1	1.0	Heptane Spray	Low	3:19
124	Vertical	Low	G-2	35	2	1	6.0	Diesel Spray	Low	0:30
125	Vertical	Low	G-2	35	2	1	3.0	Diesel Spray	Low	1:01
126	Vertical	Low	G-2	35	2	1	1.0	Diesel Spray	Low	1:03
127	Vertical	Low	G-3	7	2	1	6.0	Diesel Spray	Low	2:40
128	Vertical	Low	G-3	7	2	1	6.0	Diesel Spray	Low	No
129	Vertical	Low	G-3	18	2	1	6.0	Diesel Spray	Low	0:45
130	Vertical	Low	G-3	18	2	1	3.0	Diesel Spray	Low	1:15
131	Vertical	Low	G-3	18	2	1	1.0	Diesel Spray	Low	3:35
132	Vertical	Low	G-3	18	2	1	6.0	Heptane Spray	Low	0:51
133	Vertical	Low	G-3	18	2	1	3.0	Heptane Spray	Low	2:04
134	Vertical	Low	G-3	18	2	1	1.0	Heptane Spray	Low	1:20
135	Vertical	Low	G-3	18	2	1	1.0	Diesel Pan	Low	0:07
136	Vertical	Low	G-3	18	2	1	1.0	Diesel Pan	Low	0:09

Test No.	Nozzle Spray Direction	Grid Location	Nozzle	Pressure (bar)	Nozzle Dist (m)	Nozzle Spacing (m)	Fire Size (MW)	Fire Type	Fire Location (Figure 5)	Exting. Time (min:sec)
137	Vertical	Low	G-3	18	2	1	1.5	Heptane Pan	Low	0:09
138	Vertical	Low	G-3	18	2	1	1.5	Heptane Pan	Low	0:12
139	Vertical	Low	G-1	7	2	1	1.5	Heptane Pan	Low	0:35
140	Vertical	Low	G-1	7	2	1	1.0	Diesel Pan	Low	0:06
141	Vertical	Low	G-1	7	2	1	6.0	Heptane Spray	Low	1:21
142	Vertical	Low	G-1	7	2	1	3.0	Heptane Spray	Low	2:46
	Vertical	Low	G-1	7	2	1	1.0	Heptane Spray	Low	No
144	Vertical	Low	G-1	7	2	1	6.0	Diesel Spray	Low	0:35
145	Vertical	Low	G-1	7	2	1	3.0	Diesel Spray	Low	1:00
146	Vertical	Low	G-1	7	2	1	1.0	Diesel Spray	Low	2:14
147	Vertical	Low	G-4	70	2	2	6.0	Heptane Spray	Low	No
148	Vertical	Low	G-6	70	2	2	6.0	Heptane Spray	Low	No
149	Vertical	Low	G-6	70	2	2	6.0	Diesel Spray	Low	No
150	Vertical	Low	G-6	70	2	2	6.0	Diesel Spray	Low	0:50
151	Vertical	Low	G-6	70	2	2	3.0	Diesel Spray	Low	0:48
152	Vertical	Low	G-6	70	2	2	1.0	Diesel Spray	Low	1:32
153	Vertical	Low	G-6	70	2	2	1.0	Diesel Spray	Low	2:55
154	Vertical	Low	G-6	70	2	2	1.0	Diesel Spray	Low	2:53
155	Vertical	Low	G-6	70	2	2	1.0	Diesel Spray	Low	2:51
156	Vertical	Low	G-6	70	2	2	6.0	Heptane Spray	Low	0:46
157	Vertical	Low	G-6	70	2	2	3.0	Heptane Spray	Low	1:05
158	Vertical	Low	G-6	70	2	2	1.0	Heptane Spray	Low	1:37

Pan fires of diesel of heptane were easily extinguished during this evaluation. This was independent of the fire location or nozzle array location. Ninety percent (19/21) of the pan fires were extinguished. Extinguishment was usual within 30 seconds of mist activation. Spray fires were more difficult to extinguish. Only sixty percent (42/68) of the spray fires were extinguished.

Large spray fires were easier to extinguish than smaller spray fires. This may be related to the higher entrainment rates' characteristic of the larger fires (re-entrainment of combustion gases and steam). The heptane spray fires were slightly more difficult to extinguish than the diesel fuel. This can be attributed to the lower flash point of the heptane.

The fine water mist systems showed better extinguishment properties when the nozzles were above the fires spraying vertically down on the fire. With this configuration, 90 percent of the spray fires were extinguished verses 5 percent for horizontally spraying nozzles mounted to one side. This result can be attributed to the system redirecting a portion of the vitiated gases and steam back into the combustion zone. This creates a localized lower oxygen concentration at the combustion zone.

Some observations noted during the tests were that any areas of lower/inadequate mist concentrations (and possibly lower velocity) would prevent a system from extinguishing a spray fire. When nozzles were moved away from the fire, mist concentration holes would develop and poor extinguishment capabilities were noted. Likewise when the nozzles moved closer to the fire, the fire would extend through the mist/nozzles and burn on the backside (no mist) of the nozzle grid.

The vertically downward spraying nozzle systems were evaluated at two elevations. One directly below the test compartments overhead and 2 m below the overhead. Although the compartment was well ventilated (20 air changes per hour) a thin upper layer formed as the gases and smoke traversed to the exhaust stack. When the nozzles were directly below the overhead they would entrain some of these products and direct them into the combustion zone. When the nozzle grid was 2 m below the overhead, there was no entrainment of this upper layer which significantly increased the time to extinguishment (that is, 4:24 verse 0:11). Entrainment of vitiated gases significantly increases extinguishment capabilities.

When the systems were unable to extinguish the fires, there was a dramatic reduction in the severity of the thermal conditions in the space. We found, based on the theoretical heat release rates of the large fires (6.0 MW) verses the measured rates using oxygen calorimetry, the mist systems reduced the fire size 10 - 50 percent depending on the system. However for all the fire sizes, the amount of energy absorbed by the mist was between 30 - 70 percent of that theoretically released by the fire. The radiation attenuated by the mist was typically 60 - 90 percent of that emitted.

Conclusion

Local application of fine water mist was found to be able provide reasonable fire protection for high risk components. Systems are highly depend on nozzle spray characteristics (drop size and momentum), nozzle spray pattern, flow rate, nozzle spacing and offset distance. Even when a system was unable to extinguish the test fire, it did provide significant energy absorption and radiation reduction. This reduction in thermal assault should aid in limiting fire spread and manual intervention.

The systems tested provide the best protection when the nozzles where located above the fire and where not obstructed. The vertical nozzle array configuration did not provide good extinguishment, but did provide thermal protection of the space.

The results of the testing are being used to formulate the United States' position for the December meeting of IMO's Fire Protection Subcommittee (FP41). A complete report of this testing and additional fine water mist evaluations can be found in Reference 4.

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A NOVEL DEVICE FOR DISSEMINATING WATER AS A THREE-DIMENSIONAL FIRE EXTINGUISHING AGENT

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BACKGROUND

It is generally believed that, because of its ability to absorb large quantities of heat, a mist of water droplets would be an excellent fire-extinguishing agent. However, a mist has two distinct disadvantages.

The first disadvantage is the fact that a water mist is a streaming agent. In order for it to work effectively the location of the fire must be known ahead of time in order to orient the system with the location in mind. The other alternative is to manually direct the mist toward the fire; however, this requires operator interaction after the fire starts, which defeats the purpose of an automatic fire-extinguishing system. In either case, to achieve maximum efficiency of the water mist, the location of the fire must be known, either before or during the event. If there is the possibility of a fire in multiple locations in a given area, then either multiple streaming agents or a three-dimensional agent is needed.

When discharged, a three-dimensional agent will flood the enclosure it is in. With this flooding effect it is more likely the agent will reach a fire that is not directly in front of the discharging nozzle. Gaseous agents such as halon 1301 and carbon dioxide (CO_2) are good three-dimensional agents. However, the ozone-depletion problems associated with halon 1301 are well known. Using CO_2, the concentrations needed to extinguish a fire are too high to consider it as a viable fire-extinguishing agent in locations that are considered occupied.

The second disadvantage of a water mist is the size of the particles. The most effective mist is one that has very small water particles. With smaller particles, the ratio of the surface area to the volume of each droplet is greater. This larger ratio increases the heat transfer rate from the flame zone to the water droplets. Increasing the heat transfer rate reduces the flame temperature faster, which in turn extinguishes the fire with less water.

However, the disadvantage of a fine mist of water droplets is the ability to spray the mist. Water droplets are not very aerodynamic, and the smaller the particles the less mass they have. Nonaerodynamic, low-mass droplets make it difficult to propel a fine mist of water very far. This requires the designer of the fire-extinguishing system not only to know where the location of the fire is but also to locate the system close to the anticipated flame zone.

INTRODUCTION

A device that is capable of making and dispersing a water mist throughout a volume has been constructed. Therefore, the water mist can act as a three-dimensional agent, much like gaseous agents. The purpose of this device is to disseminate fine droplets of water in such a way as to make the droplets permeate an enclosure.

The device consists of two equally pressurized cylinders, fast-acting solenoid valves, a mixing chamber, and the necessary hardware to complete the system. One cylinder contains a vaporizable liquid, such as FE25 or CO_2, and the second cylinder contains a liquid agent such as water or a water-based solution. The cylinder containing the water is pressurized with CO_2 or nitrogen. Upon activation of the solenoid valves, two liquid streams (CO_2 and water/water-based solution) are directed into a static mixing chamber, such as a vortex mixer. The two streams are blended intimately in the chamber. Upon exiting the mixer, into a nozzle, the vaporizable liquid flash evaporates and expands throughout the volume of the enclosure. This expanding gas carries droplets of the liquid agent with it as it permeates the volume. The droplets of liquid act as the principal fire-extinguishing agent.

The vaporizable liquid (in the gaseous state) can contribute to the fire-extinguishing process; however, its main purpose is to act as a carrier for the liquid fire-extinguishing agent. This limits the amount of vaporizable agent required to the amount needed for dissemination. This will allow use of the vaporizable agent in small enough quantities that it does not exceed the No Observed Adverse Effects Level (NOAEL). The high aerodynamic drag of the small droplets is an advantage, as they are swept along by the expanding gas as it moves throughout an enclosure.

DESCRIPTION OF DEVICE

An illustration of the device is shown in Figure 1. For the purpose of experimentation, the device consists of two sections, a stationary section that is permanently connected to the experimental chamber and a removable section.

The removable section consists of two modified 15-lb fire extinguishers. The standard head and valve assembly is removed from the bottles. It is replaced with a modified system which consists of a gate valve, an overpressure disk for safety reasons, and a union for quickly disconnecting the cylinders from the stationary portion of the system for refilling purposes.

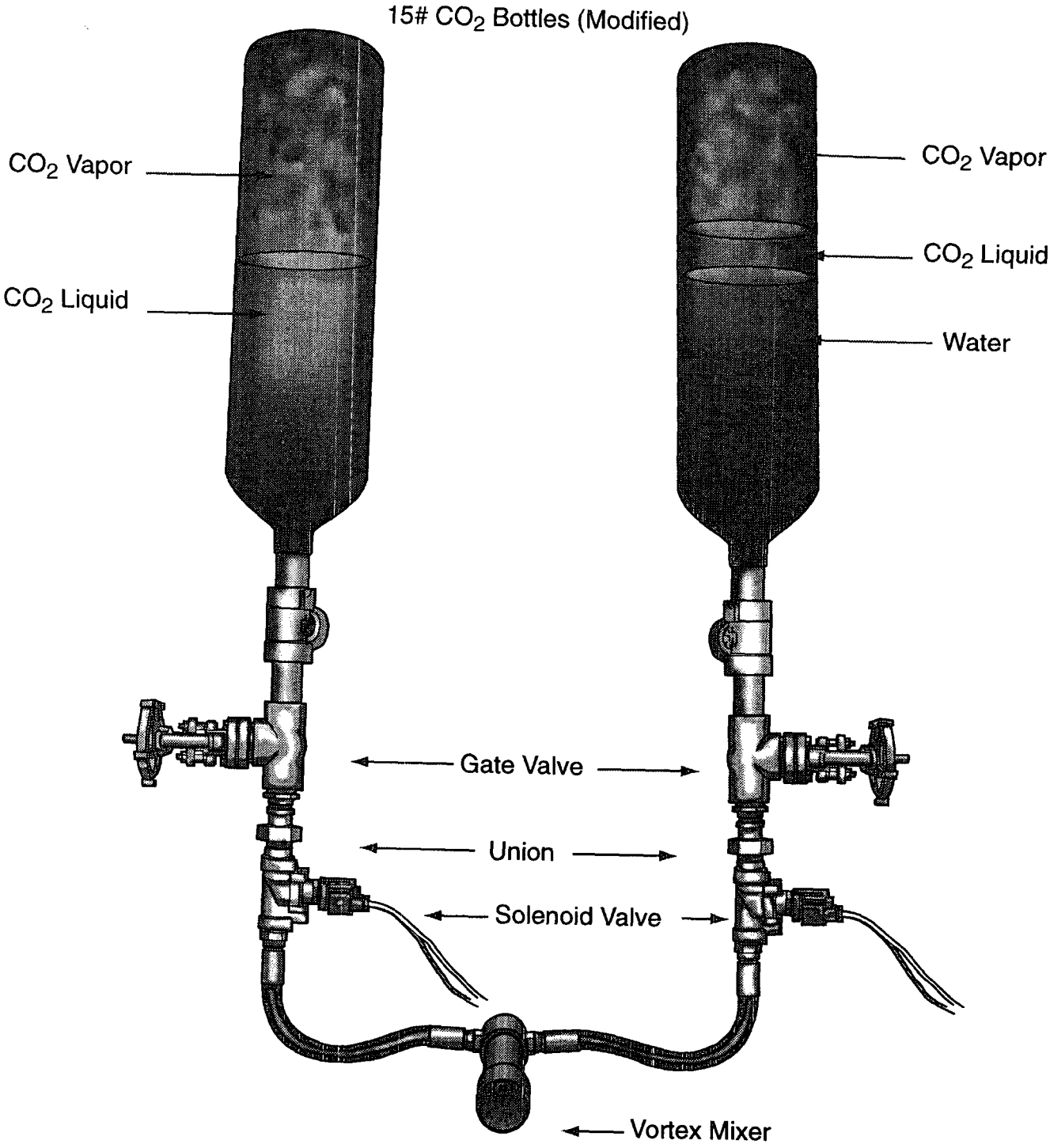

Figure 1 Illustration of Experimental Device

The valving system on both cylinders is identical. Directly out of the cylinders is a 1-inch-diameter stainless steel nipple. This nipple leads into a 1-inch stainless steel tee. In the other two sections of the tee are another one inch nipple and a stainless steel plug. The plug is modified to receive a copper burst disk that will rupture if there is an overpressure in the cylinder. The disk used is a standard disk from a 15-lb carbon dioxide fire extinguisher. The 1-inch nipple leads into a cast-iron gate valve. The gate valve is used to seal the cylinder after it is filled yet it does not restrict the flow when in the fully open position. Following the gate valve are two reducers that reduce the diameter from 1-inch to ¾ inch and then to a ½ inch. A ½-inch nipple follows the reducers and leads into the male end of a disconnect union. This union is used to simplify disassembling the system after each experiment in order to refill the cylinders.

The stationary portion of the system starts at the female end of the union. Following the female end of the union is a fast-acting solenoid valve. The solenoid valve is followed by a ½-inch flexible hydraulic hose. The hydraulic hoses from both the cylinders lead into a mixing chamber.

That is the initial configuration of the system. However, future experiments include the investigation of mixing chambers with diameters larger than a ½ inch. This will require modifications of the system beyond the gate valve.

MIXING CHAMBER

The static (motionless) mixer is the location where the two liquids (CO_2 and water) are mixed. Both liquid CO_2 and water enter the mixing chamber as two distinct streams. Within the chamber, the two streams are intimately mixed to produce a homogeneous mixture. This homogeneous mixture then exits the mixing chamber into a nozzle, where the CO_2 flash vaporizes, creating a fine mist of water throughout the CO_2 gas.

Various static mixers will be utilized to determine the characteristics of each chamber. One device to be utilized is an interfacial surface generator (ISG) motionless mixer available from Ross Engineering. This is an in-line mixer that consists of individual mixing elements enclosed in a housing. Four holes are bored in each element to allow for the flow, and the ends of the elements are machined to create a tetrahedral chamber between two elements. Within the tetrahedral chamber, the exit holes of one element are in a linear array 90° from the linear array of the entrance holes of the adjoining element. This operation of the mixer is illustrated in Figure 2.

This particular mixer offers mathematically predictable layer generation. The layer generation is the number of layers created at the exit side of an element. As an example, this device has two inlet streams entering four holes in the first element. Exiting the first element will be eight layers. Now eight layers are entering four holes in the second element. At the exit of the second element will be 32 layers.

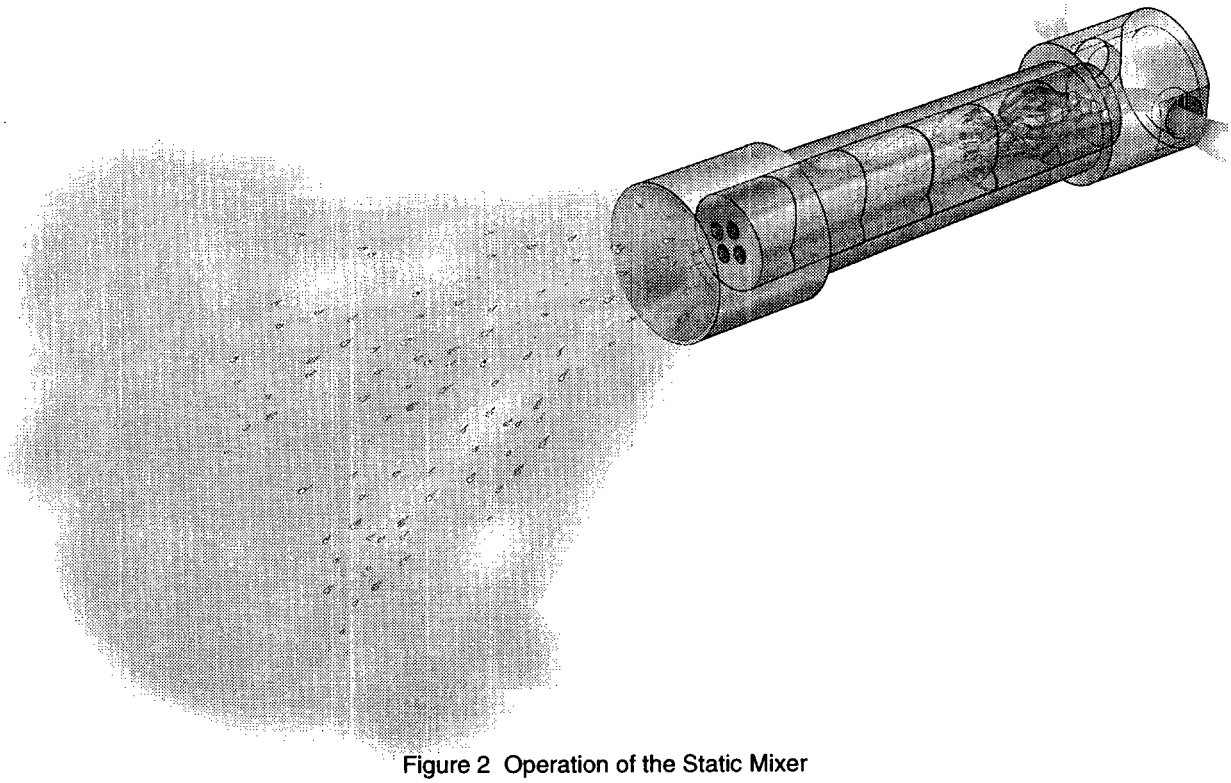

Figure 2 Operation of the Static Mixer

The number of layers emerging from an element are calculated based on the formula[1]

$$L=N(4)^E$$

Where

L = number of layers created,
N = number of initial input streams (two for this device), and
E = number of elements.

The number of elements in the array will be varied in order to determine how the number of layers created affects the output of the device. As a starting point, five elements will be used, which will yield 2,048 layers.

$$L = 2*(4)^5 = 2{,}048 \text{ layers}$$

These mixers are available in various diameters. As stated previously the initial installation will have five ½-inch-diameter elements. Variations of the mixing chamber will include changing the number of elements and using different diameter elements.

Other mixing chambers are commercially available. Motionless mixers other than the ISG mixer will be investigated to determine their effectiveness with this device.

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[1] Ross Engineering, Inc. Literature, Ross Engineering, Inc., 32 Westgate Blvd. Savannah, GA 31405-1475

CONCEPT OF DEVICE

The concept of the device is to store liquid CO_2 and water (or a water-based material) in separate cylinders. When the fire-extinguishing agent is needed, liquid water and liquid CO_2 are mixed in the mixing chamber. Upon exiting the chamber, the CO_2 flash evaporates and fills the enclosure as it normally would when released into an enclosure. However, the liquid mixture also contains water or a water-based liquid. As a result of the flash vaporization of the CO_2, a fine mist of the water/water-based liquid is created. The large aerodynamic drag associated with a fine mist of water will now be a benefit. Typically the large aerodynamic drag of a water mist is a disadvantage because it is hard to propel very far. However, in this case the CO_2 is expanding and filling the enclosure at the same time the fine mist is being created. As a result of the large aerodynamic drag, the CO_2 will carry the water mist with it as it expands throughout the enclosure.

In order to accomplish this objective one cylinder is filled with CO_2. This cylinder is inverted as shown in Figure 1 in order for the liquid CO_2 to exit the cylinder through the valving system and into the mixing chamber. The water/water-based solution is added to the second cylinder. After the water is added, the cylinder is pressurized with CO_2. This cylinder is also inverted in order for the water/water-based solution, which is denser than CO_2 to exit the cylinder.

DATA COLLECTION

Various parameters of the device will be modified to determine the optimum configuration. For the various parameters extensive data will be collected for comparison of the different configurations. The data that will be collected will include the droplet size, the droplet distribution with respect to location and time, the concentration of CO_2 in the enclosure, etc.

In order to collect these data, several tools will be used. The first data collection tool is a set of conventional drying tubes. Drying tubes will be placed throughout the enclosure to measure the quantitative amount of water at a given location. A schematic of the drying tube setup is shown in Figure 3.

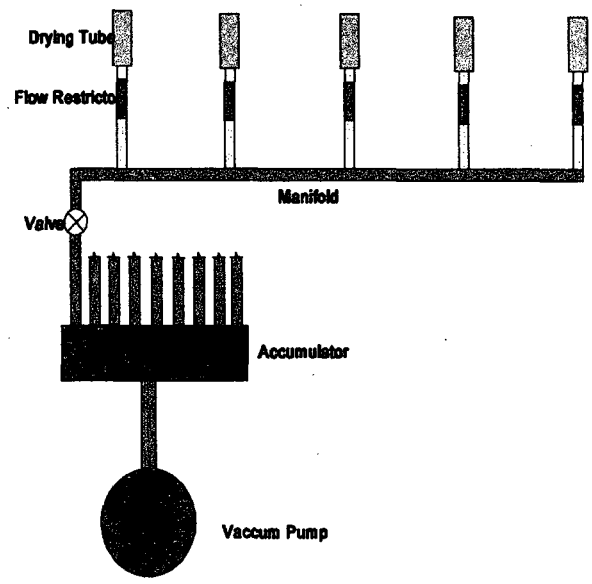

Figure 3 - Drying Tube Schematic

The drying tubes will collect data from five locations within the enclosure. At each location there will be 9 drying tubes, for a total of 45 drying tubes per experiment. This will allow for the determination of water concentration at five locations at nine different time intervals. This will indicate the concentration of water immediately

after discharge of the cylinders and at interval times following the discharge of the cylinders.

The setup consists of a drying tube filled with an absorbent material and porous plugs. The weight of the drying tube is measured prior to the experiment. Following the drying tube is a calibrated flow restricter. The flow restricter limits the flow of air to a manageable amount with respect to the vacuum pump, which is further downstream of the flow. Tubing is connected to the flow restricter, which leads into a manifold. Nine of these drying tube setups lead into a single manifold. At the beginning of the manifold is a solenoid valve. This valve starts or stops the airflow to the nine drying tubes.

A single manifold contains five drying tubes. These drying tubes are located at five separate data collection stations within the enclosure. This manifold system with drying tubes is repeated nine times. This yields 45 drying tubes, which is 9 drying tubes at each of 5 locations. The nine manifolds are connected to a central accumulator which is connected to a vacuum pump.

To obtain the data, the vacuum pump is constantly running during an experiment. After discharge of the system, the individual valves for the manifolds are opened and closed at predetermined times. Based on the time a given valve is open and the flow rate, the volume of air traveling through the drying tube is calculated. The drying tube is weighed after the experiment and compared to its weight prior to the experiment to determine how much water was absorbed. With this information, the weight of water droplets in the air can be calculated. This enables air sampling for water concentration at five different locations at nine different times. With this information a direct comparison of the water concentration can be plotted as a function of time and as a function of location.

In order to determine droplet size microscope slides will be utilized. The slides will be coated with a thin layer of silicon grease to help collect the water droplets. A device to expose these slides for a given amount of time and then cover them is being designed and constructed. It is intended to be used for future experiments. Droplet sizes have not been measured in any of the experiments described in this paper.

DISCHARGE RATES TO EXTINGUISH FIRES IN THE DESIRED TIME FRAME

The weight of water droplets per volume to extinguish a fire has been estimated using many assumptions. A conservative (high) estimate would be about 500 mg of liquid water per liter of air.

In the crew compartment of a generic military vehicle, seven pounds of halon 1301 are discharged to give an average concentration of 7% halon 1301 in air. This allows for the loss of agent due to the normal losses from the compartment. A 7% concentration is equivalent to 469 mg of halon 1301 per liter of air. This is approximately the weight of water required per liter. Therefore, approximately 7 pounds of water would be required. This is equivalent to 3.2 liters.

If a low freezing point solution, such as a 60 weight-percent potassium acetate in water solution, is used instead of neat water, considerable less agent will be required. Prior work has indicated that sprays of a 60 weight-percent solution of potassium acetate in water or a 60 weight-percent solution of potassium lactate in water is 10 to 20 times more effective than neat water at

extinguishing JP-8 pan fires.[2] Both solutions have a freezing point of approximately –60°C. It is quite possible that as little as 1 liter of solution would be required.

With this data it is conceivable that only 2 liters of liquid (one liter of solution and one liter of liquid CO_2) would be required to flow through the mixer. Current regulations require an extinguishment time of 250 ms in an occupied compartment. It takes 7 lbs of halon 1301 approximately 110 ms to discharge through its nozzle. To determine the required ISG mixer size for turbulent flow that will accommodate this flow rate the following formula[3] is used

$$\Delta p = \frac{1.2x10^{-1} Q^2 (spgr) \mu^{0.055}}{D^4}$$

Where

Δp = pressure drop across one element
Q = volumetric flow rate, gallons/minute
spgr = specific gravity
μ = absolute viscosity
D = Inside diameter of mixer housing (inches)

With CO_2, approximately 740 psi vapor pressure is available at room temperature. Using a five element 3" ISG mixer with CO_2 a flow rate of 1194 liters/min can be obtained. This correlates to 19.9 liters/s or 50.2 ms to discharge a liter. Therefore two liters can be discharged through a 3" mixer in 100.4 ms. This leaves approximately 150 ms to extinguish the fire and still be within the 250 ms required time frame.

EXPERIMENTAL SETUP

The device illustrated in Figure 1 is mounted on the inside wall of a test chamber. Rough dimensions of the test chamber are 12' x 15' x 15'. The nozzle as shown is 27 ½" above the floor of the test chamber. There are five locations where the drying tubes are located in order to measure the concentration of water in the air. All of these locations are at the same height above the floor as the nozzle. The locations are illustrated in Figure 4.

EXPERIMENTAL RESULTS

Initial experiments have been performed to test the system. All of the initial experiments have been performed with a half-inch mixer. This mixer was used instead of the 3" mixer outlined in

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[2] Finnerty, A. E., McGill, R. L., Slack, W. A., "Water-Based Halon Replacement Sprays," ARL-TR-1138, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, July 1996

[3] Ross Engineering, Inc. Literature, Ross Engineering, Inc., 32 Westgate Blvd. Savannah, GA 31405-1475

an effort to characterize the system and various parameters. A system with the 3" mixer is being designed in order to achieve the desired discharge times.

For the initial tests both of the fire-extinguishing bottles were filled with 15-lbs of CO_2. Upon activation of the solenoid valves, the two bottles discharged. The time required to discharge the bottles was approximately 45 s. This was using the system as described with the ½-inch diameter ISG mixer with five elements present.

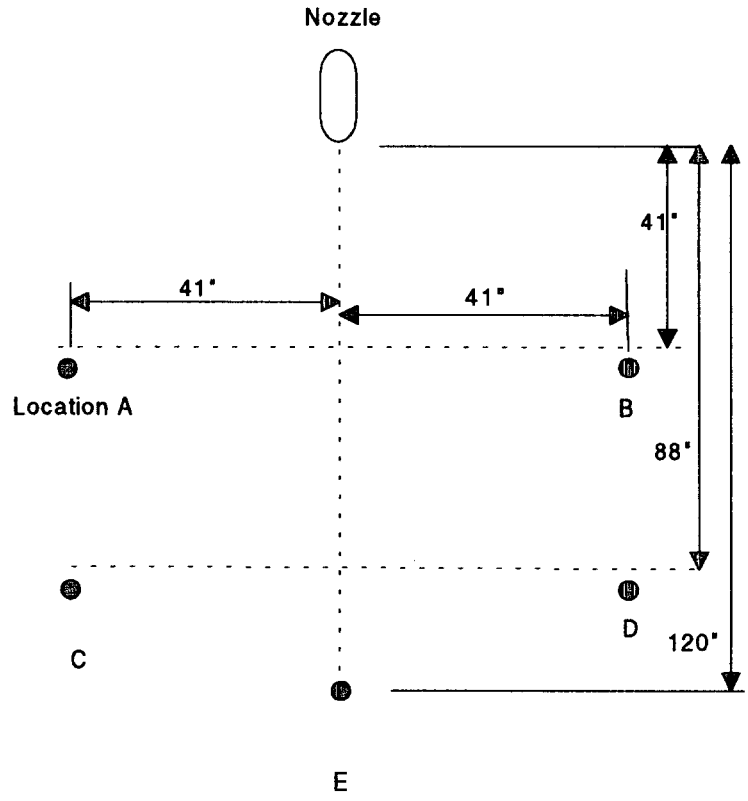

Figure 4 - Drying Tube Locations

The temperature of the CO_2 was also measured as it exited the nozzle. The minimum temperature was -65°C. As expected with this temperature, it is possible the water could freeze at some point, creating a temporary blockage in the system. For this reason experiments with a low-freezing-point water-based material are also planned.

One experiment has been performed with eight pounds of CO_2 in one cylinder and one gallon of water in the other cylinder. The second cylinder was pressurized with two pounds of CO_2. In this experiment, the vacuum was opened to draw from the first set of drying tubes, one tube at each of the five locations, for the first ten seconds after the solenoids were opened. After ten seconds, the vacuum line was closed and simultaneously opened for the second set of drying tubes. This process was continued until all nine sets of drying tubes were opened for ten seconds and then closed. Measurements of the drying tube setup gave a flow rate through each tube of approximately 6200 cc/min. For ten seconds, this gives a total flow of approximately one liter of air.

A preliminary evaluation of the data indicates that from zero to ten seconds there was little or no increase of the water in the air. From twenty to forty seconds, drying tubes three and four, the concentration of water in the air increased and then it dropped off after forty seconds. During the highest concentrations there was approximately 37 mg of water per liter of air. This is well below the desired result, but for a first experiment it shows promise.

Carbon dioxide was also measured during this test. Concentrations peaked at six percent. Based on calculations, if ten pounds of CO_2 were evenly distributed throughout the chamber the concentration would equal 2.2%. This indicates the CO_2 is not being distributed throughout the chamber uniformly. A possible cause for this could be because of the extremely low temperatures

reached when the CO_2 discharges. This could cause the CO_2 to settle quicker than it normally would and not fill the upper areas of the chamber.

FUTURE WORK

Future work will entail determining the most effective configuration. This will require experimenting with different mixing chambers. The ½-inch diameter ISG will be used. Work is currently underway to implement the 3" mixer in order to discharge the system in the desired time. The number of mixing elements will also be varied to determine how the number of layers created affects the dispersion of the water mist.

Various commercial static mixers are available. Different mixers will be investigated to determine their ability to create a mixture suitable for use with this device. Nozzle design will also be investigated to determine how the nozzle affects the output of the water mist.

Other parameters of the device will also be varied to determine the optimum configuration. Gases other than CO_2 will be investigated to determine their ability to pressurize the water/water-based solution. A possible gas for this purpose is nitrogen. Vaporizable liquids other than CO_2 for use as the propelling agent will also be investigated. One possible vaporizable liquid is FE25 due to its favorable normal boiling point, approximately that of halon 1301

After the preliminary investigation of mixing chambers, nozzle designs, various gases, etc, tell-tales fires will be created throughout the enclosure and the system will be discharged. The device's ability to extinguish the tell-tale fires will be noted. This will be repeated with the configurations that looked promising based on the data collection from the investigation of the system parameters.

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September 5, 1997

Several factors come into play when fabricating servicing equipment for Halon Replacement Agents used in fire extinguishers and systems. These factors influence the proper answer to the frequently asked question, "Why can't we use the same Recovery/Recharge/Recycling/Reclaim equipment we used for Halon 1211 or Halon 1301?" Sometimes the answer for a particular agent is "you can", and sometimes it is, "you can't". The major factors affecting the decision are given below.

Elastomeric seals that may be suitable for halons, which can be classified as non-polar solvents, will not be suitable for use with polar solvent-type agents. Unsuitable, incompatible seals will swell and stress-crack resulting in major leakage. The agent and elastomeric seals and plastic components must be compatible with the agents being processed.

The total service pressure of the agent or agent and pressurizing gas affects equipment design. Halon 1301 recycling machines have a pressure reducer at the inlet which is set to prevent pressures over 500 psig from entering the machine. The most predominantly used filter and housing unit in fire equipment and refrigeration recycling equipment has a maximum service pressure of 500 psi. Halon 1301 system pressure exceeds 500 psig, but Halon 1211 fire equipment pressures do not exceed 500 psig; therefore, a pressure reducer is not needed.

The boiling point and the freezing point of an agent dictate machine control requirements. To efficiently remove the agent gas/mixture from an extinguisher or system cylinder, the agent temperature should be above its boiling point by a reasonable amount. When a vacuum is pulled on the container, a very high efficiency agent recovery is accomplished.

Separation of the pressurizing gas from an agent is done by a cold temperature cryogenic procedure. To separate pressurizing gas from the agent in order to meet specification or to achieve efficient agent storage, the agent temperature must be significantly below its boiling temperature. Halon 1301 has a boiling temperature of -70°F (-55°C) where its vapor pressure equals 14.7 psia (one atmosphere). To achieve a high 99+% Nitrogen removal without halon loss, the agent gas temperature must be below -110°F (-78°C). Halon 1211 boils at 23°F (-10°C). Both agents freeze at approximately -256°F (-160°C). Because of the low freezing temperature, the same

Nitrogen separation system can be used for either agent. Much different temperature control points would be used to separate pressurizing gas from some other halon replacement agents.

In summary, the major factors requiring different servicing equipment when handling halon replacement agents are: seal compatibility; total storage pressure; and the temperature characteristics, boiling and freezing points of the agent.

Mr. Tom Cortina, Executive Director of HARC has compiled a very handy up-to-date list of Halon Replacement and Halon Alternative Agent Manufacturers and System Hardware Manufacturers. It is the July, 1997, Special Edition of *Harc News* which is included at the end of this report by courtesy of the Halon Alternatives Research Corporation. It contains a listing of Acceptable Halon Alternatives (and Replacements) under EPA's SNAP Program.

I recommend you call the agent manufacturer or hardware manufacturer to find out about halon replacement agent service and maintenance equipment that has been tested and evaluated for use with a particular agent. Some agent manufacturers have developed their own special units. Others recommend use of classic-type halon recovery/recharge/recycling/reclaim equipment. Some recommend using refrigeration industry transfer equipment.

The information shown below was obtained from the halon replacement agent manufacturers. Please refer to the *HARC News* for the complete address and phone/FAX numbers for each agent manufacturer.

<u>American Pacific</u>
Halotron, Inc
Agent: HCFC Blend B(Halotron 1)

Charging Equipment:

Amerex Fire International
Vice President of Sales
P. O. Box 81
Trussville, AL 35173-0081 U.S.A.
Phone: (205) 655-3271
FAX: (205) 655-3279
All international inquiries

Getz Manufacturing
Mr. Dan Sights
1525 S. W. Adams
Peoria, IL 61602-1709 U.S.A.
Phone: (309) 674-1723
FAX: (309) 673-6088
Canada, Mexico, U.S.A.

Or call Jeff Gibson at American Pacific for more information regarding charging equipment.

<u>Newhouse International, Inc.</u>
Agent: CF_3I(Triodide)

Call for information regarding charging equipment.

DuPont Fluoroproducts
Agents: HFC-23(FE-13); HFC-125(FE-25); HFC236fa(FE-36)

Charging Equipment:

Amerex Fire International
Vice President of Sales
P. O. Box 81
Trussville, AL 35173-0081 U.S.A.
Phone: (205) 655-3271
FAX: (205) 655-3279
All international inquiries

Getz Manufacturing
Mr. Dan Sights
1525 S. W. Adams
Peoria, IL 61602-1709 U.S.A.
Phone: (309) 674-1723
FAX: (309) 673-6088
Canada, Mexico, U.S.A.

North American Fire Guardian
Agents: HCFC Blend A(NAF S-III); HCFC Blend C(NAFP-III); HCFC Blend D (Blitz III); NAF P-IV™

Charging Equipment:

National Refrigeration Products, Model LV 20
1950 Street Road
Bensalem, PA 19020
Phone: (215) 639-5885
FAX: (215) 639-5765

3M
Agents: C_3F_{14}(CEA614); C_4F_{10}(CEA-410), C_3F_8(CEA-308)

Call for information regarding charging equipment

Great Lakes Chemical
Agent: HFC-227ea(FM200)

Charging Equipment:

Amerex Fire International
Vice President of Sales
P. O. Box 81
Trussville, AL 35173-0081 U.S.A.
Phone: (205) 655-3271
FAX: (205) 655-3279
All international inquiries

Getz Manufacturing
Mr. Dan Sights
1525 S. W. Adams
Peoria, IL 61602-1709 U.S.A.
Phone: (309) 674-1723
FAX: (309) 673-6088
Canada, Mexico, U.S.A.

As the demand builds, we expect an increase in the variety and capability of halon replacement agent Recovery/Recharge/Recycling and Reclaim equipment.

HARC NEWS

Halon Alternatives Research Corporation July 1997, SPECIAL EDITION

ALTERNATIVES TO HALON FOR SPECIAL HAZARD FIRE PROTECTION

The January 1, 1994 phaseout of halon production has had a dramatic impact on the protection of special hazards against fire and explosion. Halons were clean, non-conductive, safe for people, and highly effective. Replacing them in their many applications continues to present challenges for fire protection professionals.

Alternatives are now available for the majority of halon uses. The purpose of this paper is to provide a brief review of the types of alternatives that are available and to provide manufacturer/vendor information on specific alternatives.

TYPES OF HALON ALTERNATIVES

Traditional Fire Protection Agents - The use of traditional, non-halon fire protection materials such as dry chemical, CO_2, water sprinklers, and foams to protect special hazards has been promoted as a means of replacing halon use. The degree to which these traditional, not-in-kind alternatives can successfully replace halon will depend upon the details of the hazard being protected, the characteristics of the alternative method, and the risk management philosophy of the user. The U.S. Environmental Protection Agency (EPA) suggests that these materials be given serious consideration as appropriate halon replacements, but points out that they are not effective on all types of fires and should be used in specified applications as directed by manufacturers and NFPA standards.

Halocarbon Agents - These are chemical agents that contain chlorine, fluorine, or iodine either individually or in some combination. Classes of agents include hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and fluoroiodocarbons (FICs). These agents share several common characteristics, with the details varying between chemicals. These common characteristics include the following: all are electrically non-conductive, all are clean agents (vaporize readily and leave no residue), and all are liquefied gases or compressible liquids.

Inert Gases - Inert gas systems are designed to reduce the ambient oxygen concentration in a protected space to between 10 - 14%, a level that is breathable but will not support flaming combustion. These systems use inert gases such as argon and nitrogen, either as mixtures or alone. Inert gases are electrically non-conductive, clean agents.

Water Mists - Water mist systems extinguish fires using small amounts of water released as tiny droplets, under low, medium, or high pressure. These systems use specially designed nozzles to produce much smaller droplets than are produced by traditional water-spray systems or conventional sprinklers. The smaller droplets are more effective at extinguishing fires, therefore, less water is needed.

Powdered Aerosols - A category of new technologies being developed and introduced are those related to fine solid particulate and aerosols. The different types of powdered aerosol systems include pyrotechnically generated aerosols and dry chemical/halocarbon agent mixtures. Another unique category of fine particulate technology is gelled halocarbon/ dry chemical suspensions.

TABLE OF ACCEPTABLE ALTERNATIVES

Under its Significant New Alternatives Policy (SNAP) program, the U.S. EPA is required to evaluate alternative chemicals and processes intended to be used in place of ozone-depleting substances to ensure that they are acceptable from a human health and environmental perspective. EPA also places use conditions or use limits on certain alternatives, which are usually based on environmental or toxicological concerns. EPA's acceptable listing does not provide information on the suitability of an alternative in any application.

The National Fire Protection Association (NFPA) has published a standards document for halon alternative agents used in total flood systems. "NFPA 2001-Standard on Clean Agent Extinguishing Systems" contains design, installation, inspection, test, and use information on halocarbon and inert gas alternatives. The NFPA has also published a standard on water mist systems: NFPA 750 – Standard for the Installation of Water Mist Fire Protection Systems.

The table presented on page 4 provides a list of the alternatives currently considered acceptable under EPA's SNAP program and/or currently listed in NFPA 2001.

2111 WILSON BOULEVARD SUITE 850 ARLINGTON, VA 22201 (703) 524-6636 FAX: (703) 243-2874 E-MAIL:harc96@aol.com

HALON ALTERNATIVE MANUFACTURERS

3M ⊗
John Chorba
3M Center Building, 223-6S-04
St. Paul, MN 55133-3223
612-736-7569
612-736-8643 (fax)
jechorba@mmm.com
C_6F_{14} (CEA-614); C_4F_{10} (CEA-410); C_3F_8 (CEA-308)

ADI Technologies, Inc.
Jerry Brown
1487 Chain Bridge Road, Suite 204
McLean, VA 22101
703-734-9626
703-448-8591 (fax)
Powdered Aerosol A (SFE)

American Pacific Corporation ⊗
Halotron, Inc.
Pete Gibson
3770 Howard Hughes Parkway, Suite 300
Las Vegas, NV 89109
702-735-2200
702-735-4876 (fax)
Halotron@APFC.com
HCFC Blend B (Halotron 1)

Ansul Fire Protection
David Pelton
1240 Iroquois Drive, Suite 102
Naperville, IL 60563-8537
630-305-5700
630-305-3360 (fax)
dpelton@tyco.geis.com
IG-541 (Inergen)

AES International Pty Ltd
Peter Saad
9 Gloucester Road, Hurstville
P.O. Box 694, Hurstville
NSW 2200 Australia
612-9586-3200
612-9586-3211 (fax)
Powdered Aerosol C (PyroGen)

International Management Services Corp.
Joseph Brown
8298 D Old Courthouse Road
Vienna, VA 22182
703-448-4487
703-847-5430 (fax)
Powdered Aerosol C (Soyuz)

Firefreeze International
Stephanie Giessler
270 Route 46 East
Rockaway, NJ 07866
201-627-0722
201-627-2982 (fax)
Surfactant Blend A (ColdFire 302)

DuPont Fluoroproducts
Daniel Moore ⊗
Chestnut Run Plaza
P.O. Box 80702
Wilmington, DE 19880-0702
302-999-3287
302-999-2816 (fax)
daniel.w.moore@usa.dupont. com
HFC-23 (FE-13); HFC-125 (FE-25); HCFC-124 (FE-241); HFC-236fa (FE-36); HCFC-123 (FE-232)

Ginge-Kerr as
Ole Bjarnsholt
111, Stamholmen
DK-2650 Hvidovre
Denmark
IG-55 (Argonite)

Great Lakes Chemical ⊗
Doug Register
P.O. Box 2200
West Lafayette, IN 47906
317-497-6382
317-463-2849 (fax)
fm-200sales@fm-200.com
HFC-227ea (FM-200)

Minimax GmbH
Wolfgang Koch
Industriestrasse 10/12
23840 Bad Oldesloe, Germany
49-4531-803443
49-4531-803500 (fax)
IG-01 (Argon)

North American Fire Guardian ⊗
Elio Guglielmi
700 West Pender Street, Suite 304
Vancouver, BC Canada V6C1G8
604-684-7374
604-684-7415 (fax)
naftgt@hostec.com
HCFC Blend A (NAF S-III); HCFC Blend C (NAF P-III); HCFC Blend D (Blitz)

Primex Aerospace Company
Jerry White
11441 Willows Road, NE
Redmond, WA 98073-9709
206-885-5000
206-882-5747 (fax)
jdw@redm.primextech.com
Inert Gas/Powdered Aerosol Blend

Newhouse International, Inc.
Steve Newhouse
HTL/KinTech Division ⊗
111 Bayshore Avenue
Long Beach, CA 90803
562-987-1948
562-930-0329 (fax)
102052.2254@compuserve,com
CF_3I (Triodide)

Powsus Inc.
Harry Stewart
1178 Wisteria Drive
Malvern, PA 19355
610-647-2267
610-648-0793 (fax)
Gelled Halocarbon/Dry Chemical Suspension (PGA)

⊗ **Halon Replacement Agents**

Halon-like, clean, evaporating, liquefied gas, electrically nonconductive agents

SYSTEM HARDWARE MANUFACTURERS

Water Mist Systems

Fenwal Safety Systems
Joseph Senecal
700 Nickerson Road
Marlboro, MA 01752
508-429-3190
508-429-2990 (fax)

Fike Protection Systems
Jeff Moore
704 South 10th Street
Blue Springs, MO 64015
816-229-3405
816-229-4615 (fax)

Grinnell Corporation
Roger Wilkins
1467 Elmwood Avenue
Cranston, RI 02910
401-781-8220
401-781-7317 (fax)

Marioff Oy
Victor Gameiro
400-30 Berlioz
Ile Des Soeurs, Verdan (QC)
H3E 1L3 Canada
514-768-9219
514-768-5352 (fax)

Reliable Automatic Sprinkler Company
Kathy Slack
12748 Coopers Lane
Worton, MD 21678
410-778-0484
410-778-0857 (fax)

Securiplex Inc.
Maher Hanna
549 Ave Meloche
Dorval, Quebec Canada H9P 2W2
514-633-1000
514-633-8338 (fax)

Yates Fire Protection
H. James Yates
P.O. Box 9206
Hampton, VA 23670
757-827-8696
757-827-8697 (fax)

Halotron 1 (HCFC Blend B)

Buckeye Fire Equipment Company
George Reilly
110 Kings Road
Kings Mountain, NC 28086
704-739-7415
704-739-7418 (fax)

CEA-614 (C_6F_{14})

Amerex Corporation
Frank McDonough
7595 Gadsden Highway
P.O. Box 81
Trussville, AL 35173-0081
205-655-3271
205-655-3279 (fax)

Inergen (IG-541)

Ansul Fire Protection
Jim Murphy
1240 Iroquois Drive, Suite 102
Naperville, IL 60563-8537
708-305-5700
708-305-3360 (fax)

Argotec (IG-01)

Minimax GmbH
Wolfgang Koch
Industriestrasse 10/12
23840 Bad Oldesloe, Germany
49-4531-803443
49-4531-803500 (fax)

NAF S-III (HCFC Blend A)

S.E.S. Cease Fire
Ken Easey
Unit #5, 80 Citizen Court
Markham, Ontario Canada
905-415-0400
905-415-0401 (fax)

Flag Fire Equipment
Dean Doster
Highway #2 & Patillo Road
Tecumseh, Ontario Canada N8N 2L9
519-727-6722
519-727-3177 (fax)

FM-200 (HFC-227ea)

Fike Protection Systems
Jeff Moore
704 South 10th Street
P.O. Box 610
Blue Springs, MO 64013
816-229-3405
816-229-4615 (fax)

Chemetron Fire Systems
Steve Dmitrovich
4801 Southwick Drive
Third Floor
Matteson, IL 60443
708-283-4401
708-748-2847 (fax)

Kidde-Fenwal, Inc.
Carla Pizzarello
400 Main Street
Ashland, MA 01721
508-881-2000
508-881-8920 (fax)

Metalcraft, Inc.
Ernie Ellis
9331A Philadelphia Road
Baltimore, MD 21237
410-687-5500
410-687-5503 (fax)

CEA-410 (C_4F_{10})

Pem All
Don Applegate
39A Myrtle Street
Cranford, NJ 07016
908-276-0211
908-276-8074 (fax)

Modular Protection Group
Richard Niemann
5916 Dearborn Street
Mission, KS 66202
913-384-2566
913-384-5935 (fax)

FE-241 (HCFC-124)

Fireboy-Xintex
Keith Weldy
P.O. Box 152
Grand Rapids, MI 49501-0152
616-454-8337
616-454-8256 (fax)

FE-13 (HFC-23)

Kidde-Fenwal, Inc.
Mark Wickham
400 Main Street
Ashland, MA 01721
508-881-2000
508-881-8920 (fax)

FE-36 (HFC-236fa)

Ansul Fire Protection
Pete Matulonis
1240 Iroquois Drive, Suite 102
Naperville, IL 60563-8537
708-305-5700
708-305-3360 (fax)

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TABLE 1

ACCEPTABLE HALON ALTERNATIVES UNDER EPA'S SNAP PROGRAM

Streaming Agents

Agent	Comment
HCFC Blend B (Halotron I)	See additional comments 3,4. See use restrictions A.
HCFC - 123	See additional comments 3,4. See use restrictions A.
C_6F_{14} (CEA-614)	See additional comments 3,4. See use restrictions A, C.
HCFC Blend C (NAF P-III)	See additional comments 3,4. See use restrictions A.
HCFC Blend D (Blitz III)	See additional comments 3,4. See use restrictions A.
HCFC-124 (FE-241)	See additional comments 3,4. See use restrictions A.
CF_3I	See additional comments 3,4. See use restrictions A.
HFC-227ea (FM-200)*	See additional comments 3,4. See use restrictions A..
HFC-236fa (FE-36)*	See additional comments 3,4. See use restrictions B.
Gelled Halocarbon/Dry Chemical Suspension (PGA)	Allowable in residential applications.
Water Mist	Potable water, natural seawater
[Surfactant Blend] A	Not clean agent, but can reduce quantity of water needed to extinguish a fire.
Carbon Dioxide, Dry Chemical, Water, Foam	

Total Flooding Agents

Agent	Comments	NFPA 2001
HFC-227ea (FM-200)	See additional comments 1,2,3,4.	Yes - occupied areas
C_4F_{10} (CEA-410)	See additional comments 1,2,3,4. See use restrictions C	Yes - occupied areas
HCFC Blend A (NAF S-III)	See additional comments 1,2,3,4.	Yes - occupied areas
HFC-23 (FE-13)	See additional comments 1,2,3,4.	Yes - occupied areas
IG-541 (Inergen)	See additional comments 1, 2.	Yes - occupied areas

Additional Comments

1. Must conform with OSHA 29 CFR 1910 Subpart L Section 1910.160 of the U.S. Code.
2. Per OSHA requirements, protective gear (SCBA) must be available in the event personnel must reenter the area.
3. Discharge testing and training should be strictly limited only to that which is essential to meet safety or performance requirements.
4. The agent should be recovered from the fire protection system in conjunction with testing or servicing, and recycled for later use or destroyed.

Use Restrictions

A. Non-residential use only.
B. Acceptable in non-residential uses when manufactured using any process that does not convert perfluoroisobutylene (PFIB) directly to HFC-236fa in a single step.*
C. Acceptable where other alternatives are not technically feasible due to performance or

C_4F_{10} (CEA-410)	See additional comments 1,2,3,4. See use restrictions C	Yes - occupied areas
HCFC Blend A (NAF S-III)	See additional comments 1,2,3,4.	Yes - occupied areas
HFC-23 (FE-13)	See additional comments 1,2,3,4.	Yes - occupied areas
IG-541 (Inergen)	See additional comments 1, 2.	Yes - occupied areas
HFC-125 (FE-25)	Unoccupied areas See additional comments 1,2,3,4.	Yes - unoccupied areas
HCFC-124	Unoccupied areas See additional comments 1,2,3,4.	Yes - unoccupied areas
CF_3I	Unoccupied areas See additional comments 1,2,3,4.	Yes - unoccupied areas
IG-55 (Argonite)	See additional comments 1,2.	Yes - occupied areas
IG-01 (Argon)	See additional comments 1,2.	Yes - occupied areas
C_3F_8 (CEA-308)	See additional comments 1,2,3,4. See use restrictions C.	No
HCFC-22	Unoccupied areas See additional comments 1,2,3,4.	No
HFC-134a	Unoccupied areas See additional comments 1,2,3,4.	No
HFC-236fa (FE-36)*	See additional comments 1,2,3,4. See use restrictions D.	Yes - occupied areas
Water Mist	Potable water, natural seawater	See NFPA 750
Inert Gas/Powdered Aerosol Blend (FS 0140)	Unoccupied areas only. See additional comment 2.	Not applicable
Gelled Halocarbon/Dry Chemical Suspension (PGA)	Unoccupied areas only. See additional comment 2.	Not applicable
Powdered Aerosol A (SFE)	Unoccupied areas only.	Not applicable
Powdered Aerosol C (PyroGen)	Unoccupied areas only.	Not applicable
Carbon Dioxide		Not applicable
Foam A		Not a clean agent, but a low-density, short duration foam.
Water Sprinklers		Not applicable

*Proposed

convert perfluoroisobutylene (PFIB) directly to HFC-236fa in a single step.*

C. Acceptable where other alternatives are not technically feasible due to performance or safety requirements:

a. due to their physical or chemical properties, or

b. where human exposure to the extinguishing agents may result in failure to meet use conditions or in other unacceptable health effects under normal operating conditions.*

D. Acceptable when manufactured using any process that does not convert perfluoroisobutylene (PFIB) directly to HFC-236fa in a single step, for use in explosion suppression and explosion inertion applications, and for use in fire suppression applications where other non-PFC agents or alternatives are not technically feasible due to performance or safety requirements:

a. due to their physical or chemical properties, or

b. where human exposure to the extinguishing agents may result in failure to meet use conditions or in other unacceptable health effects under normal operating conditions.*

1997 International Conference on
Ozone Protection Technologies
Nov 12 - 13, 1997

NAVY HALON 1211 ALTERNATIVE STUDY

William Leach
Aircraft Fire Protection Team Leader
Naval Air Warfare Center

Daniel P. Verdonik
Hughes Associates, Inc.

NAVY HALON 1211 ALTERNATIVE STUDY

- Navy Responsible Use Policy
  - Application to All Halons
    - Use Minimization / Recycling
    - Define/Establish Strategic Reserve
    - Investigation of Alternatives
  - Particular to Halon 1211
    - Requirements Definition

NAVY HALON 1211 ALTERNATIVE STUDY

- Study Objectives
  - Alternative Development Status
  - Mission Critical Reserve Evaluation
  - Use Minimization
  - Requirements Review

NAVY HALON 1211 ALTERNATIVE STUDY

- Alternative Development Status
  - Centered on Drop-In Replacement
  - Informal "Requirements"
    - Unrelated to Particular Threat
  - Pursuit of Single Agent to Satisfy All Applications
  - No Acceptable Candidates Identified

NAVY HALON 1211 ALTERNATIVE STUDY

- Mission Critical Reserve Evaluation
  - Ship-board and Shore-based Inventories
    - Installed Base
  - Historical Usage Determination
  - Future Use Projection

NAVY HALON 1211 ALTERNATIVE STUDY

- Use Minimization
  - No Discharge During Training
    - Training Simulator
  - Enhancements to Recycling Efficiency
  - Inadvertant Discharges

NAVY HALON 1211 ALTERNATIVE STUDY

- Requirements Review
  - Individual Hardware Analysis
    - Piece-by-piece Evaluation
    - Unique Fire Threat Definition
  - Suppression Effectivity Analysis
    - Historical Fire Incidents
  - Alternate Agent Testing
    - Preliminary Assessment of Dual Agent Requirement
  - Assess "As Good As Halon" Objective

NAVY HALON 1211 ALTERNATIVE STUDY

- Products of Study
  - Technology Assessment
  - Defined System Requirements
  - Specific Hardware Assessments
  - Recommended Hardware Modifications

ADVANCES IN THE DEVELOPMENT OF STREAMING AGENTS

Mark L. Robin
Great Lakes Chemical Corporation
1801 Highway 52 NW
West Lafayette, IN 479069

Ernest E. Ellis
MetalCraft, Inc.
9331A Philadelphia Road
Baltimore, MD 21237

ABSTRACT

While significant progress has been made towards the replacement of Halon 1301 in total flooding fire suppression applications, little progress has been made in the development of viable alternatives for streaming applications. We report here the development of a novel, zero ODP extinguishing system suitable for streaming applications. Discharge testing and fire suppression performance, including performance in standard Underwriters Laboratories streaming tests are described in detail.

INTRODUCTION

During the past 30 years, the use of the highly efficient, clean, nontoxic Halon fire suppression agents has prevented the loss of human life, and these agents currently protect billions of dollars worth of equipment worldwide. However, because of their implication in the destruction of stratospheric ozone, the production of Halons was banned commencing on January 1, 1994. As a result, intensive research efforts have been undertaken in the industrial, academic, and governmental sectors with the goal of developing replacements for these agents. This paper reviews efforts in the area of streaming agents, and discusses the current status of potential replacement agents with regard to their regulatory agency approval. The development of a novel, zero ODP extinguishing system suitable for a streaming applications is also discussed, including Underwriters Laboratories fire suppression performance, and possible ground-based vehicle applications.

STREAMING AGENTS: PREVIOUS STUDIES

The fire suppression characteristics, environmental impact and toxicology of HCFC-123 (CF_3CHCl_2) and HCFC-123 containing blends have been extensively studied. Rochefort, et. al., demonstrated rapid extinguishment and demonstrated the effectiveness of HCFC-123 in the extinguishment of Class B military fire scenarios [1,2]. Following laboratory-scale investigations of fire suppression by the cup burner and the Laboratory-Scale Discharge Extinguishment (LSDE) apparatus [3], field testing of candidates on JP-4 pool fires up to 150 sq. ft. was performed under the sponsorship of the United States Air Force. These early investigations, including the examination of HCFC-123 and several

HCFC-123 based blends, indicated that HCFC-123 could meet the needs of the USAF with respect to fire suppression performance, but concerns over its toxicity led to further investigations involving the C_4 through C_6 perfluorocarbons [4]. These field scale tests in turn demonstrated that only n-C_5F_{12} and n-C_6F_{14} had sufficient volatility to be employed as streaming agents, with the best performance observed with the n-C_6F_{14} compound, perfluorohexane [5].

Perfluorohexane is characterized by a long atmospheric lifetime (3100 years) and a relatively high halocarbon global warming potential (HGWP = 5200 for a 100 year integrated time horizon). There are currently no scheduled production bans on perfluorocarbons, but SNAP guidelines restrict the use of perfluorocarbons to applications where no other alternatives are technically feasible due to safety or performance requirements.

Despite further field testing of both HCFC-123 and perfluorohexane, Air Force groups meeting at Tyndall AFB in April of 1994 concluded that no near-term candidate was completely acceptable, and that the Air Force would retain Halon 1211 until a suitable replacement became available [5].

CURRENT CANDIDATE STREAMING AGENTS

Halogenated fire suppression agents currently approved for use as streaming agents under the US EPA Significant New Alternatives Policy (SNAP) are shown in Table I. Under current SNAP guidelines, PFCs such as FC-5-1-14 are acceptable for nonresidential use only when other alternatives are not technically feasible. HCFCs are currently scheduled for phase out by 2030. The environmental characteristics of candidate streaming agents are compared in Table II, and Table III compares the current restrictions on the streaming candidate agents.

As the regulatory noose has tightened with passing time, it become apparent that a viable long term replacement for Halon 1211 would be required to have a zero ODP, and hence cannot contain chlorine or bromine. It should be noted that for the agents listed in Table I, the first five agents contain chlorine, and hence are scheduled for phaseout.

As can be seen from the Tables, the only candidate agents not scheduled for phase out due to their non-zero ODP are FC-5-1-14, HFC-236fa and HFC-227ea. FC-5-1-14, a perfluorocarbon, is subject to use restrictions based upon its long atmospheric lifetime and high GWP, and under SNAP can be employed only where other alternatives are not technically feasible.

Table I. Streaming Agents Acceptable Under SNAP

Agent	*Formula*	*Trade Name*	*SNAP Acceptability*
HCFC-123	CF_3CHCl_2	DuPont "FE-232"	acceptable
HCFC-124	CF_3CHClF	DuPont "FE-241"	acceptable
HCFC Blend B	a	American Pacific "Halotron I"	acceptable
HCFC Blend C	b	NAFG[c] "NAF P-III"	acceptable
HCFC Blend D	d	NAFG[c]"Blitz"	acceptable
FC-5-1-14	$n\text{-}C_6F_{14}$	3M Co. "CEA 614"	acceptable[e]
HFC-236fa	$CF_3CH_2CF_3$	DuPont "FE-36"	acceptable[f]
HFC-227ea	CF_3CHFCF_3	Great Lakes "FM-200"	acceptable[g]

[a]Primarily HCFC-123.

[b]HCFC-123, HCFC-124, HFC-134a, and proprietary additive.

[c]North American Fire Guardian.

[d]HCFC-123 plus proprietary additive.

[e]PFCs acceptable only when other alternatives are not technically feasible.

[f]Restrictions in total flooding applications proposed under US EPA SNAP Subsequent Proposed Rule, May 21, 1997 [7]

[g] Proposed acceptable under US EPA SNAP Subsequent Proposed Rule, May 21, 1997 [6]

Table II. Environmental Characteristics of Streaming Agents

Agent	Tradename	Atmospheric Lifetime (years)	ODP	HGWP (100 year ITH)
HCFC -123	FE-232	1.5	0.02	93
HCFC-124	FE-241	6	0.03	480
FC-5-1-14	CEA-614	3200	0	6800
HFC-236fa	FE-36	235	0	8000
HFC-227ea	FM-200	31	0	2050

Table III. Streaming Agent Comparison: Restrictions and Availability

Agent	Tradename	Subject to Use Restrictions ?	Subject to Phaseout?
HCFC -123	FE-232	yes	yes
HCFC-124	FE-241	yes	yes
FC-5-1-14	CEA-614	yes	no
HFC-236fa	FE-36	yes[a]	no
HFC-227ea	FM-200	no	no

[a] Restrictions in total flooding applications proposed under US EPA SNAP Subsequent Proposed Rule, May 21, 1997 [6]

The toxicological and environmental properties of the remaining candidates, HFC-227ea and HFC-236fa are compared in Tables IV and V, respectively. Both agents are noted to be of relatively low toxicity. Both are characterized by zero ODPs since neither agent contains bromine or chlorine. The major atmospheric sink for both agents is the reaction with tropospheric hydroxyl radicals, and rate constants for this reaction have been experimentally measured for both HFC-227ea and HFC-236fa. The rate constant for the reaction of HFC-227ea with the hydroxyl radical has been measured by several investigators [7-9], and leads to an atmospheric lifetime of 31-42 years. The rate constant for the reaction of HFC-236fa with the hydroxyl radical has been measured by Hsu and DeMore [9] and leads to an estimated atmospheric lifetime of 231 years. The 100 year ITH HGWP for HFC-227ea and HFC-236fa have been reported as 2050 [10] and 8000 [11], respectively. Based upon concerns over the long atmospheric lifetime of HFC-236fa, the U.S. EPA has recently proposed that the same restrictions be placed upon the use of HFC-236fa in total flood applications as for the perfluorocarbon agents [6].

Table IV. Toxicological Properties of Streaming Candidates

	Halon 1211	HFC-227ea	HFC-236fa
Chemical Formula	CF_2BrCl	CF_3CHFCF_3	$CF_3CH_2CF_3$
LC_{50} (4 h, rat)	10-13	> 80	> 18.9
NOAEL (% v/v)	0.5 -1	9.0	10
LOAEL (% v/v)	-	> 10.5	15
AD_{50} (10 min, % v/v)	-	> 10.5	11[a]

[a] *J. Pharm. Exp. Therapeutics*, **86**, 197 (1946).

Table V. Environmental Characteristics of Streaming Candidates

	Halon 1211	HFC-227ea	HFC-236fa
Chemical Formula	CF_2BrCl	CF_3CHFCF_3	$CF_3CH_2CF_3$
ODP	3	0	0
k_{298} for reaction with hydroxyl radical (cm^3 $molecule^{-1}$ s^{-1})	-	1.6E-15	3.4 E-16
Lifetime (years)	15	31-42	231
HGWP (100 yr ITH)	-	2050	8000

STREAMING PERFORMANCE OF HFC-227ea

In general, lower boiling, highly volatile compounds such as HFC-227ea (bp -16.4 °C) exhibit poor performance in streaming applications and are more suitable for total flooding applications. For example, comparing Halon 1301 (CF_3Br, bp -58 °C) and Halon 1211 (CF_2BrCl, bp -3 °C), it is seen that Halon 1301 is employed primarily in total flooding applications due to its gaseous nature which allows it to completely flood an enclosure, whereas Halon 1211 is employed in portable units where a stream of agent is directed at the fire.

MetalCraft, Inc. and Great Lakes Chemical Corporation have jointly developed a novel extinguisher design which greatly enhances the performance of HFC-227ea in streaming applications. Table IV shows the results of Underwriters Laboratories testing of the new HFC-227ea unit, in this case a unit containing 2.5 pounds of HFC-227ea. In recent testing, a 3B rating has been achieved for a unit containing 3 pounds of HFC-227ea.

Table IV. UL Testing of MetalCraft/GLCC 2.5 lb Unit

Fire Type	2B	2B	2B	2B
Fire Size (ft^2)	5	5	5	5
Preburn (s)	60	60	60	60
Conditioning	Normal	Normal	Normal	-40 °F
Pressurization (psig)	360	360	360	360
Extinguishment	yes	yes	yes	yes
Agent Discharge (lb)	1.7	1.6	2.0	1.6

One possible application of the new HFC-227ea unit is in ground-based vehicle protection. The U.S. Army has recently sought a replacement for the CO_2 unit currently employed in their ground-based vehicles; the CO_2 unit itself had replaced a Halon 1301 unit. The fire suppression requirement for the U.S. Army extinguishing unit is a minimal UL 2 BC rating. Tables V through VII compare the HFC-227ea unit with both the Halon 1301 and CO_2 units. It can been seen from these Tables that the new HFC-227ea unit takes up less space and weighs considerably less than the current CO_2 unit. Comparing to the original Halon 1301 unit, it can be seen from the Tables that the new HFC-227ea unit is a drop-in for the originally employed Halon 1301 unit.

Table V. U.S. Army Ground-Based Vehicle Applications: Cylinder Comparison

	Halon 1301	CO_2	FM-200
Type	DOT 4B500	DOT 3AA1800	DOT 4B500
Material	Steel	Steel	Steel
Non-Shattering	yes	yes	yes

Table VI. U.S. Army Ground-Based Vehicle Applications Extinguisher Comparison

	Halon 1301	CO_2	FM-200
Agent Weight (lb)	2.75	2.5	2.5
Specification	MIL-E-52031D	CID52471D	MetalCraft
UL Rating	2 BC	2 BC	2BC
Height (in)	13.5	13.5	13.5
Width (in)	6.5	7.25	6.5
Diameter (in)	3.5	4.375	3.5
Total Weight (lb)	7.35	12.0	7.3
Operating Pressure (psig)	380	900	360
Operating Temperature (^{o}F)	-50 to 120	-50 to 120	-50 to 120

Table VII. U.S. Army Ground-Based Vehicle Applications Bracket Comparison

	Halon 1301	CO_2	FM-200
Static Load			
Down	200	350	350
Up	88	88	88
Out	200	200	200
Mounting	vertical or horizontal	vertical only	vertical or horizontal
Hole Pattern	same	same	same

CONCLUSION

The development of a novel extinguisher design has allowed for the extension of HFC-227ea to streaming applications. Employing the new design has allowed the achievement of 2B and 3B UL ratings for 2.5 and 3 pound units, respectively, and it is expected that further design modifications will allow the achievement of a 5B rating.

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Characterization of Flammable Liquid Storeroom Fires

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ABSTRACT

The United States Navy is investigating gaseous replacement agent and alternative technology fire extinguishing systems for future use in applications where Halon 1301 total flooding systems have traditionally been used. The Naval Research Laboratory (NRL) is conducting tests in Flammable Liquid Storerooms (FLSRs) at its Chesapeake Bay Detachment (CBD). The U.S. Navy has specific fire suppression and reignition prevention requirements. NRL has conducted extensive tests to evaluate several candidate gaseous replacement agents in shipboard applications where the main fire threat is from pressurized fluids (fuel, hydraulic oil, or lubricating fluid). The agents were tested for their ability to suppress various test fires (pool and spray), fuels (n-heptane, diesel, wood crib and cable insulation), and prevent reignitions. The chemical 1,1,1,2,3,3,3 heptafluoropropane (HFC 227ea, HFP) was recommended for use as the clean replacement agent in future construction U.S. Navy ships. In order to enhance gaseous agent performance, real scale testing has also been conducted with hybrid systems utilizing HFP and the NRL Water Spray Cooling System (WSCS).

The current research effort is to evaluate HFP for use in FLSRs. There are several important differences between machinery spaces and FLSRs, hence, there are differences in the fire suppression system design requirements. These differences include: fuels (impacts design concentration), fire type, obstructions and compartment geometry, shelving type (solid or perforated), occupancy (normally unoccupied may allow for higher design concentrations), detection and response criteria, and system activation.

The objective of these tests is to evaluate HFP, with and without WSCS, with limited Halon 1301 baseline comparisons, in a representative shipboard FLSR. This paper discusses development of realistic shipboard fire threat scenarios, use of worst case fire scenarios to hinder fire suppression (to test agent limitations), and limited test bed design considerations. Issues and limitations of halon replacement systems are also discussed.

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INTRODUCTION

The Naval Research Laboratory (NRL) is investigating fixed fire extinguishing systems for future use in Flammable Liquid Storerooms (FLSRs) where Halon 1301 total flooding systems have been used. The FLSR program is being conducted at NRL's Chesapeake Bay Detachment Facility (CBD).[1] FLSR 1 is a 28 m^3 (1,000 ft^3) test compartment. This test bed is applicable to many smaller shipboard compartments.[3] FLSR 2 will have an internal volume 280 m^3 (10,000 ft^3), a representative size for large shipboard FLSRs.

The purpose of this paper is to address the different fire scenarios that can be expected in shipboard flammable liquid store rooms as well as the selection of fire scenario particulars for the evaluation of halon replacement systems. Compartment shelving, fuel particulars, and different spill and ignition scenarios are addressed. This paper covers fuel selection and use, fire scenario particulars including compartment ventilation shutdown and preburn time selection, and test running procedures. Fire test results are given in a companion paper.[4]

DEVELOPING THE BASELINE FIRE SCENARIO

For real scale fire suppression, developing fire scenarios to simulate a particular application involves an evaluation and characterization of the following primary parameters:

- Compartment size and obstructions
- Fuel type, geometry, and location
- Ignition sources
- Detection type and response
- Fire growth curve
- Response time: elapsed time from detector activation to agent discharge initiation
- Oxygen concentration and its variation within the compartment during suppression
- Reignition potential
- Hold time: elapsed time between agent discharge and compartment reclamation
- Venting and reentry/ reclamation procedures

Identifying the realistic worst case fire scenario involves characterizing the above parameters for the application in question as well as identifying the limitations of the suppression system.

TEST COMPARTMENT

The dimensions of the Flammable Liquid Storeroom 1 (FLSR 1) were 3.05 m (10 ft) long, 3.05 m (10 ft) high from deck to overhead and 3.05 m (10 ft) wide. The enclosed volume was approximately 28 m^3 (1,000 ft^3). The forward section of the compartment was located opposite the door.

The test compartment was fitted with storage racks along the port (left) bulkhead and most of the forward bulkhead. The storage racks were composed of four levels of removable shelving sections that are approximately 66 cm (26 in) in depth. The heights at which the shelving could be positioned are 61 cm (24 in), 122 cm (48 in), 183 cm (72 in), and 244 cm (96 in).

SHELVING AND MOCKUPS

Solid and perforated shelves were evaluated since both are present in the Fleet.[2] Significant variations of the fire characteristics were observed with the different types of shelving. The perforated shelves were used as the baseline testing configuration.

Three types of mockup configurations were used (Table 1). Five gallon steel containers were used for the Limited mockup configuration. In addition to the five gallon containers the Full mockup configuration also utilized 55 gallon drums. For the different fuel flow rates used, the extent of the cascading fuel leak was characterized with both types of shelving and all three mockup configurations.

Table 1.

Mockup Configuration	Number of Containers	Mockup Volume (m^3)	Floodable Compartment Volume (m^3)
None	0	0	28.3
Limited	53	1.3	27.0
Full	126	3.5	24.8

VENTILATION

The Ventilation Supply and Exhaust Systems were set at 7.1 m^3/min (250 cfm) each. Gases were vented from the test compartment through a stack attached to the outside of the FLSR 1. Both the supply and exhaust ventilation systems (including dampers) were remotely actuated and monitored.

INSTRUMENTATION

Data acquisition and instrument/component control was performed by the Experiment Running Personal Computer (ERPC). The ERPC was a 150 MHZ Pentium system with LabVIEW Full Development System data acquisition software utilizing a National Instruments modular interface. The ERPC collected data from the compartment on over 350 data acquisition channels at frequencies of 1 Hz to 100 Hz. Instrumentation included:

- one MIDAC FTIR (with its own data acquisition and control system),
- continuous sampling of CO, CO_2, O_2 and agent concentrations, performed at four locations in the compartment,
- grab sampling, 9 locations, conducted at specified time intervals to collect agent and acid samples,
- over 40 thermocouples to measure compartment air and surface temperatures,
- smoke obscuration, measured by Optical Density Meters (ODM) at four heights,
- four video cameras (2 visible wavelength, and 2 infrared wavelength), to monitor and record the fires, fire suppression, agent and WSCS discharge.

TEST MATRIX

The FLSR 1 test matrix was comprised of 13 test series with over 80 tests. Approximately 30 tests were agent fire suppressions. The series particulars are listed in Table 2.

Table 2.

Test Matrix				
Test Series	Agent	Fires	WSCS Assisted Fire Suppression	Key Variables
1	None	Yes	No	Fire tests, no mockups, compartment door opened and closed
2	HFP	No	No	Agent discharge system nozzle locations, no mockups
3	None	Yes	No	Preburns with mockups
4	HFP	No	No	Agent discharge system nozzle locations, with mockups
5	HFP Halon 1301	Yes	No	Agent concentrations, agent
6	HFP	Yes	Yes	WSCS initiation time, WSCS application duration
7	HFP	Yes	Yes	WSCS application rate, WSCS initiation time, WSCS application duration
8	HFP	Yes	No	WSCS initiation time
9	HFP Halon 1301	Yes	Yes	Agent, WSCS initiation time
10	HFP	Yes	No	Fire size
11	HFP	Yes	Yes	Fuel
12	HFP	Yes	No	Hold Times, agent concentration
13	HFP	Yes	Yes	WSCS application rate, WSCS initiation time, WSCS application duration, door open

FIRES

Three fires were used during FLSR 1 testing. Tests were conducted with only one fire burning at a time.

Fire 1, the primary fire, was a Class B "3-D, Cascading" fire dripping through the shelving and around the mockups. Fires 2 and 3 were Class A solid fuel fires located in the forward starboard corner and center of the compartment respectively.

The Fire 1 fuel used was a mixture of 80% methanol and 20% n-heptane. Methanol was used as the primary fuel because of its very high HFP Cup Burner extinction concentration and because it is commonly found on shipboard FLSRs. Heptane was added to methanol to make the flame more visible therefore enhancing flame monitoring, as well as safety. The fuel was initially introduced at the 9 foot level over the shelving. Different fuel flows and preburn durations (Table 3) were evaluated. The higher fuel flows resulted in a significant oxygen depletion even with the shorter preburn durations. With the lower fuel flow rate, very little fuel reached the deck. In order to limit the part of the cascading fire that was immersed in the oxygen depleted overhead layer, the fuel leak was then lowered to the 5 foot level. A pan was also introduced at the deck level, where the lowest oxygen depletion occurred.

Fire ignition was achieved by electrically heated elements and lit telltales. Reignition attempts were performed with the heated elements. A small number of tests were conducted with the Full mockups configuration. This setup significantly limited the amount of oxygen available to the fire during the preburn, therefore, a Limited mockup configuration was adopted. With this configuration, mockups were placed on the shelves within the Fire 1 cascading fuel flow and on deck around the fire pan. While maintaining to a minimum the volume occupied by the mockups, the mockups were installed to obstruct the agent from getting to the fire, as well as to provide a larger surface area for the dripping fuel to flow over.

Table 3.

Fuel	Preburn Duration (min)	Fire Size (MW)	Fuel Leak Rate (lpm)
MeOH (80%) n-Heptane (20%)	1 - 3	0.2 0.3 0.4	0.05 0.075 0.1

FIRE SIZE AND COMPARTMENT SIZE

In comparing different total flooding test beds, the ratio of fire size to compartment volume alone is not sufficient to describe the severity of the fire and the degree of difficulty it will present for the fire suppression agent. Preburn duration coupled with ventilation particulars, in terms of ventilation flow rates, and fan/damper actuation timing are equally important.

The ventilation particulars of the early NRL intermediate scale halon replacement work at CBD,[3] although very challenging for the agent, did not represent a realistic small FLSR scenario but more closely resembled a manned space fire scenario. With the compartment being very well ventilated until just before agent discharge, larger fires were possible with very limited oxygen depletion.

The FLSR 1 test bed was designed to accurately simulate a shipboard compartment. Compartment layout, tightness, ventilation hardware, and agent discharge system hardware all very closely resemble a shipboard FLSR. Furthermore, test running procedures, in terms of preburn duration and agent discharge, also replicate possible shipboard event timing (see TEST RUNNING PROCEDURES). For the test beds used in NRL's Halon 1301 replacement efforts, Table 4 lists their sizes and the fires that were used in them.

Table 4.

Test Bed	Floodable Compartment Volume (m^3)	Fuel	Fire* Size (MW) (min / max)	Fire Size / Comp. Volume (min / max)
CBD Intermediate Scale[3]	56	n-Heptane	0.5 / 3	0.01 / 0.05
ex-USS SHADWELL Phase 1[5]	756 (total 840)	n-Heptane	1.6 / 7.0	0.002 / 0.01
ex-USS SHADWELL Phase 2 [6, 7]	370 (total 395)	Diesel (F-76) spray	3.3 / 4.7	0.01 / 0.013
FLSR 1	27	Methanol (80%) n-Heptane (20%)	0.2 / 0.45	0.005 / 0.017

* Primary Fire

TEST RUNNING PROCEDURES

The short term objective of the FLSR 1 Halon replacement test program is to identify the implementation particulars of HFP for use onboard the LPD-17, the U.S. Navy's next ship class.

The Navy doctrine for manual system activation along with detector activation and shipboard personnel response were evaluated to determine likely preburn scenarios. Table 5 displays the time sequence for the tests and a predicted shipboard scenario for the FLSR aboard LPD-17.

Table 4.

Event	Event Initiation and/ or Duration (min:sec)	
	CBD FLSR 1	*Shipboard (LPD-17) Scenario*
Open dampers	at test initiation	dampers are normally open
Initiate fan motors	at test initiation	fans are normally on
Fuel leak initiation	-	-
Fuel ignition by heated element	Variable (prolonged ignition will yield a larger fire, initially)	Variable: depends on leak and ignition source

"Detection"	Can be determined using LPD-17 detectors or Thermocouple simulation	Variable: depends on fire and detector
Damage Control Central response: time until dispatcher identifies fire in FLSR and activates system	Variable: shorter times will result in a tougher fire to suppress (less O_2 depletion)	Variable: (estimated) 0:15-3:00
Egress/ Ventilation Delay Initiation	0:25 minimum requirement	0:30 -1:00
secure fan motors	~0:05	0:30 - 1:00 (interlocked fan motors and dampers)
close dampers	0:20	
Discharge Agent	Variable (see Damage Control Central Response)	Variable (see Damage Control Central Response)

CONCLUSIONS

Shipboard FLSRs pose a significant problem in terms of fire protection. The fuel population is as diverse as the types of storage containers. Furthermore there is significant variability in shelving and compartment layout that greatly affects fire growth predictions.

A realistic worst case fire scenario to evaluate a halon replacement agent must include the compartment ventilation and discharge system activation particulars. Smaller FLSRs due to the limited oxygen supply and internal volume can only sustain very limited size fires.

Identifying fire out times for complex geometries is not trivial. Careful placement of thermocouples together with infrared cameras can yield a better picture of the effects of agent discharge on a 3-dimensional cascading obstructed fire. Small lingering flamelets, even though they may raise no concerns in terms of any significant fire damage, can present a significant reignition threat during compartment reentry and reclamation when fresh air is introduced and agent concentration diluted.

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Halon 1301 Replacement System Implementation for Flammable Liquid Storerooms

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TEST PROGRAM

The Naval Research Laboratory (NRL) has conducted extensive intermediate[1] and full scale [2, 3] Halon 1301 replacement tests simulating shipboard machinery spaces in which the primary fire threat is pressurized flammable liquids. Several other threat scenarios exist in Navy ships that require the use of a total flooding fire suppression system. The United States Navy is investigating fixed fire extinguishing systems for future use in Flammable Liquid Storerooms (FLSRs) where Halon 1301 total flooding systems have been used.

The program is designed to be conducted primarily in two test compartments. The FLSR 1 is a 28 m^3 (1,000 ft^3) test compartment.[4] This test bed is applicable to many smaller shipboard compartments.[3] FLSR 1 tests are also serving as a learning process for designing and executing larger scale FLSR tests. FLSR 2 will have an internal volume of 280 m^3 (10,000 ft^3), a representative size for large shipboard FLSRs.

OBJECTIVES

The FLSR 1 program had three primary objectives. The first objective of the program was to quantify 1,1,1,2,3,3,3 - heptafluoropropane (HFC-227ea, HFP) performance in terms of fire suppression, reignition protection, and quantities of agent decomposition products generated. Overall gaseous suppression system performance was characterized fas a function of agent concentration, number and placement of discharge system nozzles, effect of obstructions, and fuel and fire type. The second major goal of the program was to investigate the performance of a hybrid system utilizing HFP with a Water Spray Cooling System (WSCS), first tested on the *ex*-USS SHADWELL.[5] The WSCS, a low pressure water spray system, was primarily designed to enhance gaseous agent performance, reduce toxic byproducts, and reduce compartment

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temperatures. Various WSCS initiation times, flow rates, application durations, and number and locations of nozzles were tested. The third objective of the FLSR 1 program was to compare HFP with baseline Halon 1301 performance.

FLSR DESCRIPTION

FLSRs are unoccupied spaces where flammable liquids and materials impregnated with them are stored. A survey in the Fleet early in the test program revealed a very diverse fuel population and loading. Fuels found in FLSRs included: paints, paint thinners, alcohols, solvents, various Class A materials, drop cloths, oils (including linseed), paint brushes, and various acids. Alcohols and acids are stored in separate designated flammable liquid cabinets. Types of storage containers are as diverse as the fuels ranging from military specification to commercial off-the-shelf containers, including glass containers.

Shipboard FLSRs vary in size from less than 28 m^3 (1,000 ft^3) on smaller ships to over 1100 m^3 (40,000 ft^3) on aircraft carriers. Compartment obstructions include shelving and fuel containers (from quart size to 55 gal drums).

SUPPRESSION AGENT DESIGN CONCENTRATION

The prime agent evaluated during the FLSR 1 test program was HFP. The NRL Cup Burner was used to determine extinction concentrations (Table 1) for HFP and Halon 1301 for both methanol and the 80-20 methanol-heptane mixture used in FLSR 1 testing.

Table 1.
NRL Cup Burner Extinction Concentrations

Fuel	HFP Cup Burner (% v/v)	Halon 1301 (% v/v)
heptane	6.6	3.1
methanol	8.9	6.3
80% methanol, 20 % heptane	8.3	5.8

For FLSRs, the US Navy design concentration for Halon 1301 is 5.0% to 7.0% (by volume at 10°C). NFPA 12A, Section 3-4.1.2* also lists a minimum design concentration of 5.0% for "fires involving several flammable liquids and gases".[6] The preliminary HFP design concentration for FLSRs is 11.5% to 12% at 20°C. The overall system safety margin above Cup Burner can only be computed for specific fuels (with known cup burner extinction concentrations). Shipboard FLSRs have such a diverse fuel population that the only way to arrive at a design concentration is to identify some of the expected worst candidates for the particular suppression agent. Partly in order to reduce the fire hazard of the alcohols, the Navy isolates them in designated flammable liquid cabinets within the FLSRs.

FIRE THREAT

FLSRs pose a very different fire threat compared to machinery spaces. The primary threat in FLSRs is a cascading 3-dimensional fuel spill scenario, whereas in machinery spaces the threat is a pressurized Class B (liquid fuel, hydraulic fluid, or lubricating oil) leak. The particulars of the three fires tested in FLSR 1 are listed below. Fire 1 was the baseline fire. Only one of the three fires was used for any given test. Ignition was achieved by electrically heated elements or lit telltales.

Fire 1: 3-D Class B (80% methanol - 20% n-heptane) fire located in the forward port top corner of the compartment cascading within the shelving and a 1 ft^2 pan on deck.

Fire 2: Class A (solid fuel: cardboard) fire contained in a 2 ft x 2 ft pan located in the forward starboard corner of the compartment.

Fire 3: Class A fire located in the center of the compartment, contained in a 2 ft x 2 ft pan.

BASELINE TEST DECRIPTION

The baseline suppression test used an HFP design concentration of 11.5%. The preburn duration (time from fire ignition to agent discharge) was two minutes. Ventilation was secured 30 seconds prior to agent discharge. Compartment ventilation was reinitiated 15 minutes after agent discharge. Reignition attempts were conducted during the 15 minute hold time and during venting. The test sequence of events is listed below in Table 2.

Table 2.
Test Sequence of Events for Baseline Fire Suppression

Time (min:sec) t_0 *@ agent discharge*	*Event*
-5:00	Open dampers and initiate fan motors
-2:00	Fuel "leak" initiation
-2:00 - 1:30	Fuel ignition (delayed ignition will yield a larger fire, initially)
Variable	"Detection" can be determined using detectors or thermocouple simulation
-0:30	Secure fan motors
-0:30	Close dampers
0:00	Discharge agent
5:00, 10:00, 15:00	Reignition attempts
15:00	Venting Initiation
16:00, etc.	Reignition attempts every minute thereafter until failure

RESULTS

Oxygen depletion plays a critical role in assessing total flooding suppression agent performance.[7] This is particularly true in small enclosures with a limited initial quantity of oxygen and for systems with manual activation with prolonged preburn times. In FLSR 1 for the baseline fire scenario, the average oxygen concentration at agent discharge was 15%. In the overhead, oxygen concentrations reached the single digits. Fires in such vitiated air are much easier to extinguish. For particulars on the design of the baseline fire scenario see reference 8, "Characterization of Flammable Liquid Storeroom Fires" also presented at the 1997 International Conference on Ozone Protection Technologies.

HFP Fire Suppression

Several design concentrations of HFP were tested ranging from 9.0% to 12.5%. Suppression times were very similar for all four design concentrations (Table 3). A significant difference in time to reignition of the fire pan was observed between the low and high agent design concentrations. The high design concentration provided longer protection, i.e. longer time to reignition, as more agent had to be vented prior to reaching a low enough concentration to allow reflash.

Table 3.
Effects of HFP Design Concentration on
Fire Suppression and Reignition Performance

HFP Design Concentration (%)	Suppression Time* (min:sec)		Reignition** (min:sec)	
	Pan	Cascading	Pan	Cascading
12.5 (5.11)	0:10	0:06	20:00	17:15
11.5 (5.4)	0:10	0:07	n/a	17:40
11.1 (5.5)	0:10	0:07	19:20	17:25
10.8 (5.3)	0:10	0:08	19:23	17:30
9.0 (5.1)	0:09	0:07	18:20	17:00

* Agent discharge initiated at 0:00.
** Venting initiated at 15:00 after agent discharge

Hydrogen fluoride (HF), a toxic and corrosive gas, is the main fluorine containing agent byproduct. Carbonyl fluoride (CF_2O), which hydrolizes to form HF, is also generated. HF and CF_2O concentrations were measured using a MIDAC FTIR and several ion specific Continuous Acid Analyzers (CAAs). The CAAs use an ion specific electrode to determine the concentration of a halide anion. Due to its solubility and reactivity in the CAA aqueous solution, CF_2O is detected as it generates two fluoride anions per molecule. When comparing FTIR and CAA data, the HF values listed are the sum of HF and 2 times CF_2O peak values. HF concentrations were found to vary significantly within the compartment. As with the early intermediate scale halon

replacement work,[1] a higher agent design concentration produced a smaller HF peak concentration (Table 4).

Table 4.
Effect of HFP Design Concentration on Peak Hydrogen Fluoride

HFP Design Concentration (%)	Suppression Peak HF		Reignition Peak HF	
	FTIR (ppm)	CAA (ppm)	FTIR (ppm)	CAA (ppm)
12.5 (5.11)	1400	500*	2400	2000*
11.5 (8.1)	3100	2100	5800	5000

* CAA not sampling at the same location as the FTIR.

Enhancing the Suppression System Performance using the WSCS.

The WSCS, a NRL innovation first tested aboard the *ex*-USS SHADWELL[5, 9] was used to reduce compartment temperatures, reduce acid by-product formation, scrub acid byproducts from the ambient air, enhance reignition protection, and expedite compartment reclamation. The WSCS was a low pressure (less than 90 psi) water spraying system. Several application rates, durations, and intitation times were tested. The WSCS significantly reduced the HF generated during suppression and limited the amount generated during reignition (Table 5). The test with the WSCS in Table 8 had a WSCS application that initiated 30 seconds before agent discharge for 90 seconds and an application at venting initiation for 90 seconds. Both applications were at 4.6 gallons per minute.

Table 5.
Effects of WSCS on HF Generation

WSCS	Suppression Peak HF		Reignition Peak HF	
	FTIR[1] (ppm)	CAA (ppm)	FTIR[1] (ppm)	CAA (ppm)
No (5.10)	<400	500*	3000	2000-15000
Yes (6.2)	(800)**	<200*	850	300-9000*

* Range of several locations.
** Uncertain measurement due to water droplets interference with IR beam.

Halon 1301 Fire Suppression

Two Halon 1301 tests were conducted with the baseline test configuration. Both tests resulted in fire out times of less that 10 seconds with complete suppression of both the cascading and pan fires. Reignition times (Table 6) were comparable to the lower concentration HFP tests.

Table 6.
Effects of Halon 1301 Design Concentration
on Fire Suppression and Reignition Performance

Halon 1301 Design Concentration (%)	Suppression* (min:sec)		Reignition* (min:sec)	
	Pan	Cascading	Pan	Cascading
5.1 (5.7)	0:09	0:06	18:20	17:20
6.2 (5.12)	0:08	0:05	18:30	17:07

* Agent discharge initiated at 0:00.

Measured peak hydrogen fluoride concentrations were significantly lower with Halon 1301 than with HFP (Table 7). Hydrogen bromide concentrations (Table 8) were comparable to hydrogen fluoride.

Table 7.
Effect of Halon 1301 Design Concentration on Peak Hydrogen Fluoride

Halon 1301 Design Concentration (%)	Suppression Peak HF		Reignition Peak HF	
	FTIR (ppm)	CAA (ppm)	FTIR (ppm)	CAA (ppm)
5.1 (5.7)	500	<200*	1000	3400*
6.2 (5.12)	900	<200*	800	200-2400**

* CAA not sampling at the same location as the FTIR.
** Range of two CAAs.

Table 8.
Peak Hydrogen Bromide Halon 1301 Design Concentration

Halon Design Concentration (%)	Suppression Peak HBr		Reignition Peak HBr	
	FTIR (ppm)	CAA (ppm)	FTIR (ppm)	CAA (ppm)
5.1 (5.7)	Not detectable	200*	500	6400*

* CAA not sampling at the same location as the FTIR.

Suppression System Performance Failure

A Halon 1301 suppression test was conducted with the ventilation dampers left open for the duration of the test. An unobstructed air flow in the ventilation supply and/ or exhaust ducts can result from the lack of dampers, or from the dampers being left open due to a mechanical

failure (damper, actuator, or interlock). The test illustrates what can happen if methanol is not properly stored and there is unobstructed gas flow in the supply and exhaust ducts. During the damper open test the pan fire was not suppressed. Pan and cascading fire out times as well as reignition times for both tests (dampers open and closed) are listed below (Table 9).

Table 9.
Effects of Open Ventilation Dampers on
Fire Suppression and Reignition Performance

Ventilation Damper Configuration During Hold Period	Suppression* (min:sec)		Reignition* (min:sec)	
	Pan	Cascading	Pan	Cascading
Closed $_{(5.7)}$	0:09	0:06	18:20	17:20
Open $_{(5.7_DO)}$	Not Extinguished	0:05	(17:36)**	16:45

* Agent discharge is initiated at 0:00.
** Visible reflash, not reignition since initial pan fire was never extinguished.

HF VALUE INTERPRETATION

Typically, only the peak HF values, normally measured at a single point, have been reported in the literature. Little information has been available on the range of HF concentrations that can be expected within an enclosure as well as the HF decay. Real scale testing on the *ex*-USS SHADWELL[11] as well as testing in FLSR 1 have revealed very large HF inhomogeneities during halon replacement suppressions.

In unoccupied spaces without vulnerable equipment, the HF value of import will be the concentration just prior to venting or compartment reclamation (threat to human exposure). For the baseline HFP test, FLSR 1 HF values have been in the order of 500 ppm or less after a 15 minute hold time. With the use of the WSCS, these values were much lower and similar to those measured from the Halon 1301 baseline suppressions.

The NRL FLSR 1 reignition test is a very conservative and severe one. The high HF values observed after reignition illustrate the need for its consideration in compartment reclamation procedures.

For spaces containing electronics or other vulnerable equipment, the peak HF concentrations as well as the HF loading (ppm-minute) of exposure during the hold time is critical and has to be addressed when selecting a design concentration.

CONCLUSIONS

Due to oxygen depletion effects in small tight compartments, fires are significantly inhibited and easy to extinguish. These easily suppressed fires, together with employment of high concentrations of HFP, will generate HF quantities that pose only a small threat. The WSCS (and other water suppression systems) may be sufficient for fire suppression in small compartments. These conclusions are not expected to be valid for large compartments due to the greater amount

of oxygen that will be available for combustion.

Even with a 15 minute hold time prior to venting, significant venting will have to occur before the acid concentrations can be reduced significantly to allow the compartment to be "gas free" and personnel to enter without breathing protection. Compartment reclamation remains an issue for FLSR protection particularly due to the presence of very volatile fuels. Time between agent discharge and compartment venting, as well as ventilation rates, need to be determined. WSCS provides a very significant increase in reflash protection, even with a short application duration in advance of compartment reentry.

Selection of a design concentration for a FLSR requires an evaluation of the contents inventory. The Cup Burner or an equivalent screening tool should be used to determine the starting point in the calculation of the design concentration. A safety margin can then be added to the minimum extinction concentration. The safety margin should cover the known uncertainties as well as provide a degree of protection that matches the owner's risk aversion for the facility.

The test conducted with Halon 1301 with the dampers open illustrate the performance limitations of a very efficient agent. The replacement agent systems with their lower safety margins need to be optimized prior to being implemented.

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Laboratory Evaluation of Bicarbonate Powders as Fire Suppressants

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The Combustion Dynamics Section of the Navy Technology Center for Safety and Survivability is actively involved in addressing US Navy needs for fire protection, concentrating on the effectiveness of current and future fire extinguishing agents, with the responsibility to recommend and help design Navy shipboard total flooding fire suppression systems. We are currently examining several replacement agents and alternative suppression technologies including the use of aerosols and powders.

This paper describes recent collaborative work with Kidde International on the flame extinction properties of various bicarbonate powders. We have examined the concentration of bicarbonate powders required to extinguish both laboratory counterflow propane-air diffusion flames and small obscured n-heptane pan fires. Extinction information as a function of powder composition and size has been obtained. Within experimental uncertainty, smaller particles were more effective than larger ones. Potassium bicarbonate was more effective than sodium bicarbonate for each particle size studied. Similar dependence on size and powder composition was observed in both the counterflow diffusion flame and small chamber pan fire tests. Powder extinction data are given as well as implications of the findings.

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INTRODUCTION

The phaseout of halon production, as required by the Montreal Protocol, continues to challenge researchers to find an effective alternative to the superior fire fighting agents of the halon family. Halon 1301 has been used quite effectively in many applications where a clean agent is not absolutely required. With the phaseout of halons and the lack of a suitable backfit replacement it is now more critical to design fire protection systems appropriate for the application.

There are certainly many applications where fire extinguishment by a gaseous suppression agent is highly desired and there are halon replacement clean agents commercially available. Gaseous hydrofluorocarbon (HFC) agents and inert gases are the front runners in the race for a halon replacement, but none reach the level of overall effectiveness and safety as Halon 1301. Although HFC's cause no significant damage to the ozone layer, they do produce hydrogen fluoride, an extremely corrosive byproduct of the fire suppression process. There is still a need for an efficient and economical replacement/alternative for many spaces currently protected by Halon 1301.

Flame extinguishment by dry chemicals, most notably alkali metal salts, is not a new technology. Agents such as sodium bicarbonate have been used in hand extinguishers since the 1940's. Small particle size alkali metal salts are known to have excellent extinguishing capabilities [1], more effective on a mass basis than even gaseous agents such as Halon 1301 [2-4]. Highly efficient dry chemical agents can provide excellent fire protection while consuming minimal space.

The most common alkali metal salt agents in use are sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$). $NaHCO_3$ is widely used in fire extinguishers because of its low cost. Both agents also have markets in such applications as paint spray booths, fuel filling stations, restaurant cooking areas, and in explosion protection. In addition to high efficiency, the powders have many other advantages including low toxicity and corrosivity. The impact on the environment from $NaHCO_3$ or $KHCO_3$ is minimal. They have zero ozone depletion potential (ODP) and global warming potential (GWP). The powder left by the dry chemicals following suppression remains a drawback, limiting their application to areas that can tolerate the residue. Decreased visibility during application is also a concern. Particle suspension is another limitation, especially for applications requiring a total flooding agent. In these applications the particles must remain suspended in the fire threat area sufficiently long to eliminate the chances of a reignition. The agent must also flow around objects to extinguish obstructed fires in a similar manner to gaseous agents. For conventional sized extinguishing powders (i.e. 20-100 μm) the majority of the particles are too massive and are not capable of suspension for extended periods of time. Pyrotechnic generation [1] can yield micron sized aerosol. Also, very small, aerosol sized particles of non-pyrotechnic potassium bicarbonate powder have been developed [3] to address the questions of flow and suspension, and are currently being tested in Europe for use in scenario specific applications [5].

EXPERIMENTAL

The flame extinguishing performance of powdered agents was evaluated in a propane-air counterflow diffusion flame at NRL and in an obscured n-heptane pan fire within a fire test chamber at Kidde. Extinction testing was conducted with both sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$). Preparation of the tested samples was performed by Kidde in separate runs for both laboratories using the same method and base stock powders. Prior to particle size fractionation the $KHCO_3$ sample was ground using a ball mill (Fritsch Pulverisette type 06.102) to reduce the large chunks of powder into small enough sizes to permit sieving. Due to the lower mean particle size of the $NaHCO_3$ (Dessikarb) powder as received, it was fractionated without any prior grinding. Both powders were then mechanically sieved (Fritsch Analysette type 03.502) in a shaker to size ranges of <38 μm, 38-45 μm, 45-53 μm, 53-63 μm, and 63-75 μm. Silica (2% by mass) was

added to the powder samples as a drying/anti-caking additive. All powder samples flowed very freely with no agglomeration noticed. A scanning electron microscope (Cambridge S200) was used to examine the powdered test samples following sieving. Photomicrographs of the $NaHCO_3$ showed a very even distribution of particle sizes throughout each size range. Conversely, photomicrographs of the $KHCO_3$ showed that there was a significant percentage of very small particles (i.e. <<38 μm) in each size bin.

Experiments were conducted in a counterflow diffusion burner [6]. The counterflow diffusion flame is laminar and one-dimensional and allows for variation of the strain rate (see below). Extinction testing enables a fundamental study of the extinction mechanism and the influence of such factors as size, chemical composition, and strain rate. The burner consists of two axisymmetric, 1 cm ID burner tubes separated by 1 cm as shown in Figure 1. A flame is established in the region between the two tubes where the opposed fuel and oxidizer flows meet and diffuse. Air and propane were used for the oxidizer and fuel, respectively, with the air flow through the top and the propane through the bottom tube. The flame can be described in terms of the strain rate. The strain rate is defined as the maximum velocity gradient on the oxidizer side of the flame and has units of s^{-1}. Laser- Doppler velocimetry (LDV) is used to measure the velocity profile along the tube centerline. In an uninhibited flame, extinction is achieved when the air and fuel flow rates are increased such that the velocity gradient exceeds the critical value referred to as the *extinction strain rate*. For an uninhibited propane-air flame this has a value of 560 s^{-1}. For these flames, extinction was typically only achieved along the centerline, leaving an annular flame.

Powder concentrations for flame extinction were measured at three different flame conditions characterized by the respective flows of air and fuel. Strain rates determined for the flames using an LDV system were 180, 310, and 480 s^{-1} for what are referred to as low, medium, and high strain, respectively. For the powder extinction concentration tests, the flame was established approximately midway between the two tubes at one of the predetermined strain rates. The powder was injected and mixed into the air stream from above the flame to best simulate an actual fire suppression situation. The agent delivery system consisted of a vibrating, variable orifice device. The orifice was changed for gross adjustment and the vibration frequency for fine adjustment. The powder flow was quantified by light scattering using a modulated He-Ne laser beam just below the air exit tube. The powder scattered the laser light, which was collected by optics at 90° and processed in a lock-in analyzer synchronized to the frequency of the modulated beam. The powder flow was correlated to the light scattering by collecting and weighing powder in the absence of the flame. For flame extinction, the powder flow was introduced into the air side of the flame and gradually increased until the flame extinguished. Extinction occurred only along the centerline as in the uninhibited flame. The addition of powder to the flame dramatically increased the excited C_2 emission from the flame. A suitable optical filter was used to block this emission.

Data were collected by a computer using an analog to digital board (Scientific Solutions Lab Tender). The board was 8 bit, bipolar, with an input range of -5 to +5 volts. The data collection rate of the computer was set at 2 Hz. In addition to the He-Ne scattering signal collected by the system, a second channel recorded the intensity of the central, luminous zone of the flame as imaged into a photomultiplier tube. Extinction of the flame was marked by a dramatic decrease in the light intensity signal. The scattering signal was evaluated at the time corresponding to the flame emission decrease to determine the powder scattering signal at extinction. Calibration of the He-Ne scattering was performed following extinction measurements at each strain and for each particle size bin.

The powders were also tested in a 287 liter fire test chamber [3] modified as shown in Figure 2. The fire is obscured from above and on the sides by metal plates as shown. This test design was chosen to evaluate the total flooding ability of the powders. The suppressant tested was weighed to

0.01 g and loaded into the reservoir. It was then pressurized to 140 psig with nitrogen and dispersed through a simple nozzle (shown in insert) in the roof of the chamber. Water and n-heptane were added to the fire pan and the baffles put in place. The fire was then ignited and the chamber sealed. At 45 s after ignition the fan was switched off and the fan door closed; at t=55 s, the test chamber side vents were closed; at t=60 s, the suppressant was discharged. If the fire remained lit at t=75 s, the test was classified as a failed suppression.

For each test, fresh water and fuel were used. Between tests, the chamber was cleaned of residual suppressant. The dispersion apparatus was cleaned with a compressed air line when different particle size fractions were being evaluated to prevent cross-contamination. By changing the amount of suppressant used in the subsequent tests according to the results of those previous, it was possible to find an increasingly smaller range around the "critical" mass measured for extinction of the flame.

RESULTS

Counterflow Diffusion Flame

Extinction mass concentration measurements for $NaHCO_3$ and $KHCO_3$ powders in the air flow of a propane-air counterflow diffusion flame as a function of the measured strain for each size bin are tabulated in Table 1 and plotted in Figure 3. In general, they show that the extinction mass concentration varies inversely with the strain rate of the flame and directly with the particle size of the agent. Figure 4 is a plot of the extinction mass concentration ratio of $NaHCO_3$ to $KHCO_3$ versus strain for each particle bin size tested. The figure shows that $KHCO_3$ is approximately 2.5 times more effective than $NaHCO_3$ on a mass basis in extinguishing the flame (3 times more effective on a molar basis).

A number of factors have been postulated to contribute to the inhibition of fires by powders. The powder adds a great deal of heat capacity to the flame, and solid particles are often effective infrared radiators, leading to radiational cooling of the flame zone. In addition, some chemicals (including the alkali metal bicarbonates) [7] will undergo endothermic decomposition at elevated temperatures, releasing carbon dioxide. The residual metal hydroxide may itself vaporize and decompose at a much higher temperature. Furthermore, there exists the possibility of free radical scavenging processes involving either the solid surface of the particle (heterogeneous) or gaseous by-products of the solid's decomposition (homogeneous) [8-10].

The exact mode of the alkali metal bicarbonates' effectiveness is still not completely understood. The difference in effectiveness between sodium and potassium could be due either to differences in the decomposition temperature and enthalpy, or to differences in catalytic scavenging cycles between the two elements.

One point worth noting is that for nearly all of the possible modes of operation, the particles' effectiveness should scale with surface area. This includes heat transfer, radiation, decomposition/vaporization, and surface catalysis. Therefore small particles are expected to be more effective at fire suppression, in accord with our experimental observations. This dependence does not, however, allow us to determine the primary means by which these particles extinguish fires.

The size of the particles in the flame is an important characteristic in the effectiveness of an agent. The sooner a particle begins the decomposition phase, the sooner it can act out its role in suppressing the flame, whether it be physical or chemical. As shown in Figure 1, in a stagnation point flow field the streamlines turn radially upon impingement by the opposing flow. Particles will either follow these streamlines if small enough, or will deviate from the streamlines and begin to fall

downward for the case of particles large enough that the gravitational force overcomes the drag force imposed by the carrier gas. Thus, the residence time of each particle in the flame is a function of the trajectory that it follows and the resulting velocity. Also, the rate of heat absorption by a solid particle is proportional to its surface area and a smaller particle presents more surface area per unit mass to the flame than a large one. Within the experimental uncertainty there was an increase in extinction mass concentration (i.e. decrease in effectiveness) with increasing particle size, which has also been seen previously at NRL [1,11]. This is seen in Figure 3 for both agents.

Plots of the extinction mass concentration as a function of average particle diameter and surface area can be found in Figures 5a and 5b, respectively. The figure contains data for the medium strain case for both powders tested. The average particle diameter was calculated as the arithmetic mean of each particle size bin, assuming an even distribution. This average particle diameter was then used in the calculation of the average particle surface area. In Ref. [11], the authors concluded that the fire extinguishing effectiveness of dry chemicals can be fully explained on the basis of particle size and distribution. They found that the effectiveness of the agent increased gradually as the particle diameter decreased until reaching a critical diameter. At this diameter there was a dramatic increase in the flame suppression efficiency and the effectiveness remained constant for all particles below the limit size. The limit sizes were reported as 16 μm and 22 μm for $NaHCO_3$ and $KHCO_3$, respectively. We noticed a dramatic increase in the efficiency at about 45 μm for the $NaHCO_3$ sample at medium strain. A sizable increase was also noted for $KHCO_3$, but at a much larger particle size of about 65 μm. The higher value found for $KHCO_3$ may be influenced by the large percentage of very small particles in all size bins of this agent. The data show that the required extinction concentration increases with the diameter and surface area. A linear correlation between extinction mass concentration and diameter was not found at the medium strain tested as seen in Figure 5a. There does appear to be a linear correlation at the medium strain case for the extinction mass concentration versus average particle surface area as seen in Figure 5b. For this strain, the particle surface area available to interact with the flame more closely correlates with suppression effectiveness than does the particle diameter.

For the high and low strain cases the correlation between surface area and effectiveness was complicated by other factors. For the low strain flame, the largest particles were not suspended near the stagnation plane by the opposing fuel flow, but fell directly through the flame and into the bottom tube. A dramatic drop off in effectiveness was observed for the two largest particle bins, which may have resulted from the reduced residence time. For the high strain case, the amount of powder required to extinguish the flame was so small that the particle delivery was difficult to accurately measure and control with our seeding apparatus, leading to uncertain and poorly reproducible values. It was thus difficult to quantify a relationship between particle size and effectiveness for these two strains, but smaller particles were once again more effective. Effectiveness did correlate more closely with surface area than with diameter. Note that the determination of surface area in this study was based on the assumption of a spherical particle of the average diameter for the sieve fraction. A more accurate determination of the effect of surface area on suppression will require direct measurement of surface area (i.e. by gas adsorption). These observations are, however, consistent with "real world" experience that smaller particles are preferable due to both increased surface area and more favorable suspension properties [3].

Pan Fire Chamber Test

Extinction mass concentration measurements for $NaHCO_3$ and $KHCO_3$ powders on an obscured n-heptane pan fire in a 287 liter chamber are tabulated in Table 2 and plotted in Figure 6. The results show $KHCO_3$ to be more efficient in suppressing these fire than $NaHCO_3$. Smaller

particles are also more efficient in suppressing fires than are large particles. It is difficult to determine the dependence of surface area on the effectiveness because of the many interrelated variables affecting the chamber test results.

The extinction mass ratio (Na/K) for the two powders tested was determined to be 2.1, 2.8, and 1.9 for the size ranges of < 38 μm, 45-53 μm and 63-75 μm, respectively. The values are not monotonic with particle diameter. This may be due to the poor sieving of the $KHCO_3$ into the particular size ranges. This may also be due to the greater hygroscopicity of $KHCO_3$ compared with $NaHCO_3$. There is a great number of small particles visible in the photomicrographs of the 45-53 μm sieve fraction of $KHCO_3$, perhaps explaining the apparently much higher efficiency associated with this sample (i.e. 2.8) compared with the other two size ranges (i.e. 2.1 and 1.9). The 63-75 μm sieve fraction for $KHCO_3$ was seen to comprise some very large particles, with one axis much greater than 75 μm, and some very small particles. Though these effects will, to some extent, cancel one another, this cannot be a basis for scientific comparison.

SUMMARY

We have examined the fire suppression properties of bicarbonate powders in two different environments. Similar dependence on size and powder composition was found in both studies. $KHCO_3$ was shown to be more effective on a mass basis than $NaHCO_3$ for all particle sizes tested. It was also shown that the effectiveness of an agent varies inversely with the particle size for the ranges tested; smaller particles are more effective in suppressing the flame than the larger ones. However, the results are not readily transferable to full scale fire applications. Factors such as the throw (i.e. fire penetration), suspension, and flow as a function of particle size are all important considerations in determining the optimum particle size for each application. Additional testing is recommended to help evaluate these characteristics. Better understanding of these characteristics will help to determine the applicability of dry chemical agents as an alternative to Halon 1301.

The testing reported here is preliminary work of an ongoing collaborative effort between the Naval Research Laboratory and Kidde International. Additional testing by both is planned to better evaluate the effectiveness of powdered extinguishing agents. Experiments are underway at NRL to determine the size distribution of the samples used. Kidde is also currently involved in the assessment of particle sizes using a commercial particle analyzer. Extinction testing with better characterized particle size distributions is planned. These results will be used to gain a better understanding of flame extinguishment by dry chemicals and to help determine the characteristics of the optimum agent.

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Chemical	Measured Strain (s^{-1})	Extinction Mass Concentration for Specified Size Bin (g/m^3)				
		<38 μm	38-45 μm	45-53 μm	53-63 μm	63-75 μm
$NaHCO_3$	180	70	52	150	270	730
	310	8	15	53	56	80
	480	4	1	7	7	4
$KHCO_3$	180	12	18	70	100	370
	310	3	12	20	18	51
	480	1	6	3	1	2
Halon 1301	180	110				
	310	56				
	480	15				

Table 1: Propane-air counterflow diffusion flame extinction mass concentration for the indicated agent. Halon 1301 data derived from Ref. [12].

Chemical	Extinction Mass Concentration for Specified Size Bin (g/m^3)		
	<38 μm	45-53 μm	63-75 μm
$NaHCO_3$	52	82	130
$KHCO_3$	25	29	69

Table 2: Obscured pan fire mass extinction concentration for the indicated agent.

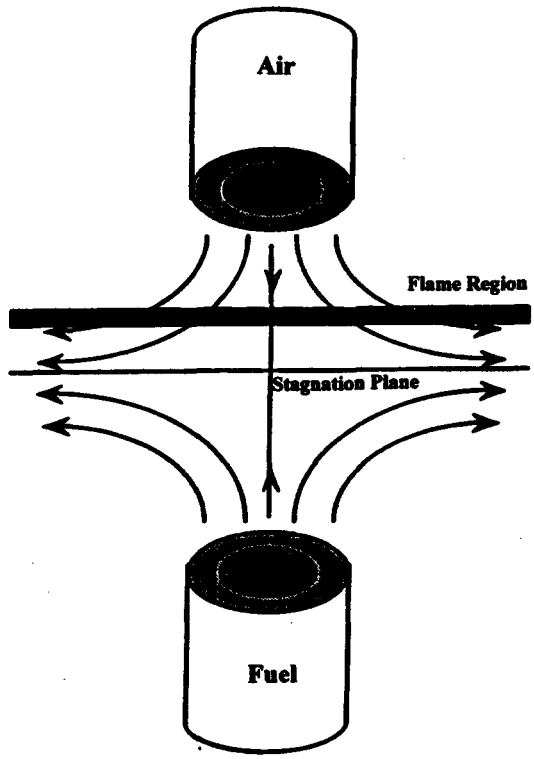

Figure 1: Schematic of the counterflow diffusion flame apparatus from Ref. [6].

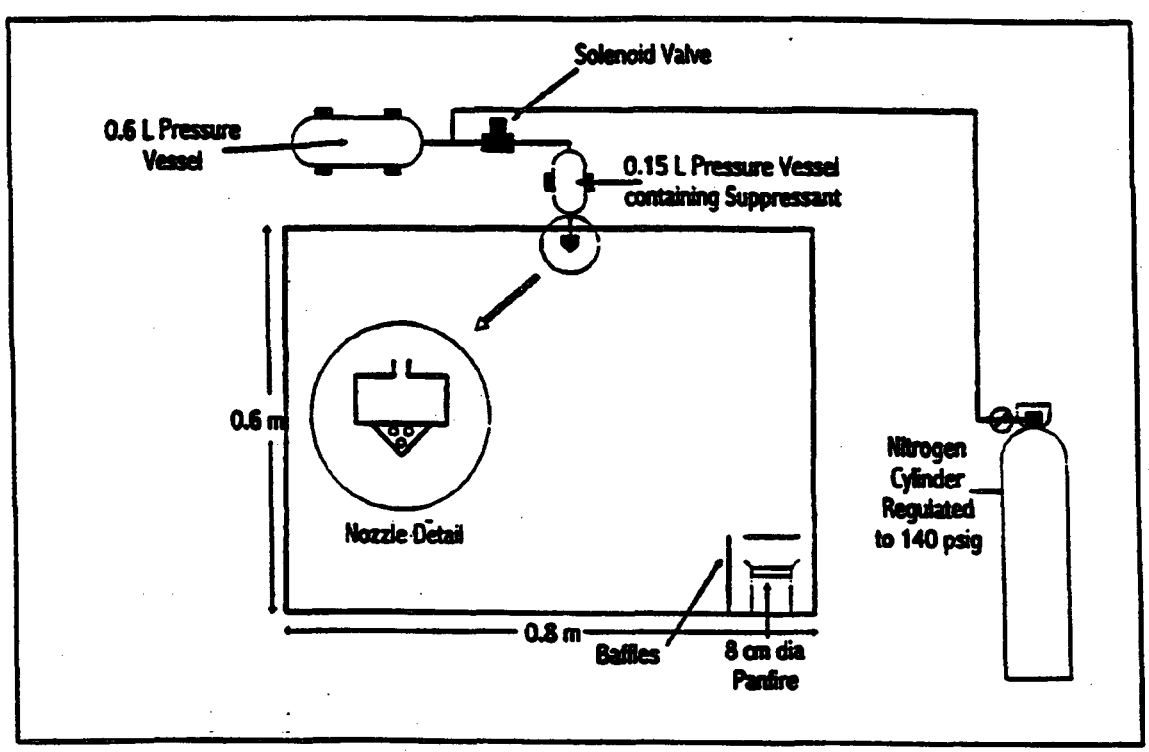

Figure 2: Schematic of 287 liter obscured fire test chamber.

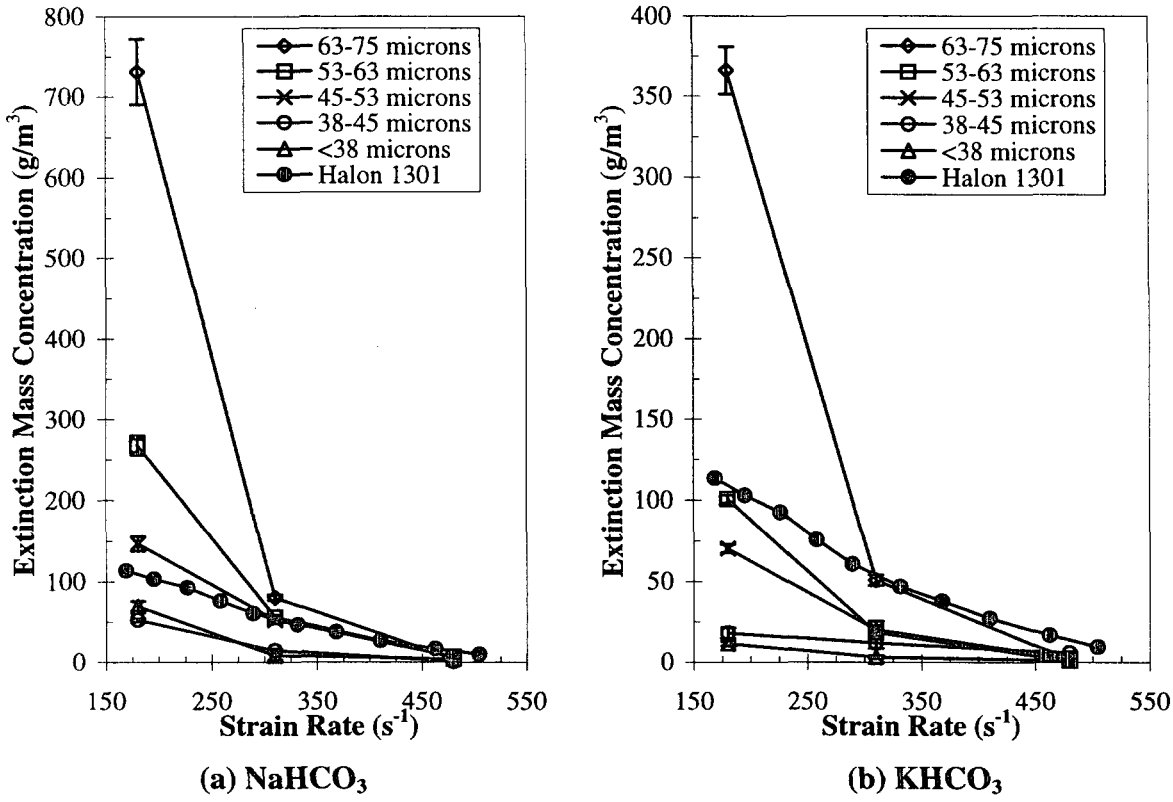

Figure 3: Extinction mass concentration as a function of strain rate for each particle size range of (a) $NaHCO_3$ and (b) $KHCO_3$ powders in a propane-air counterflow diffusion flame. Halon data from Ref. [12].

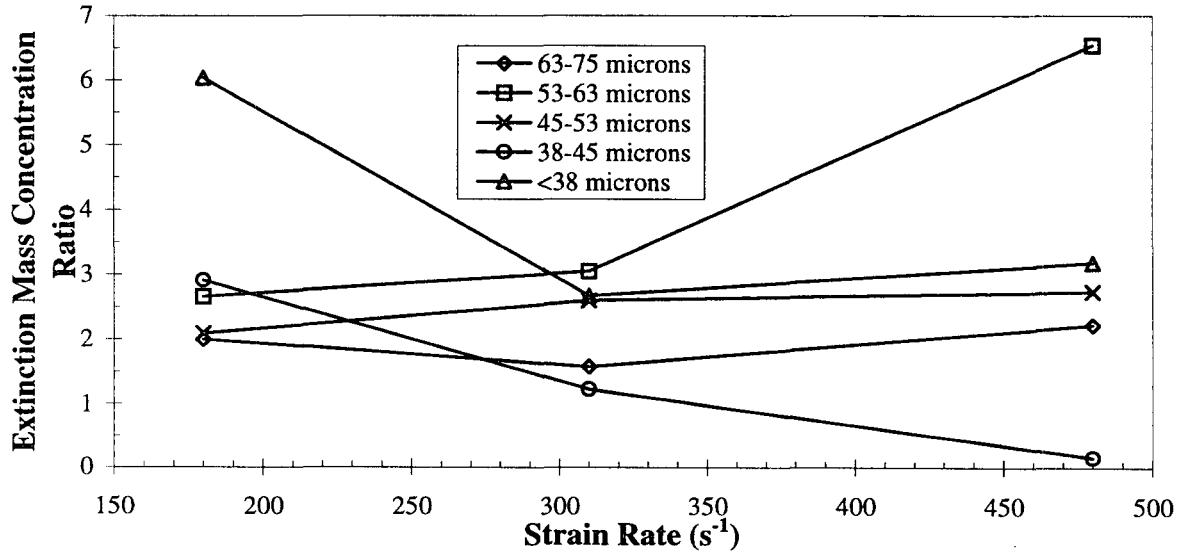

Figure 4: Extinction mass concentration ratio (Na/K) as a function of strain rate for each particle size range in a propane-air counterflow diffusion flame.

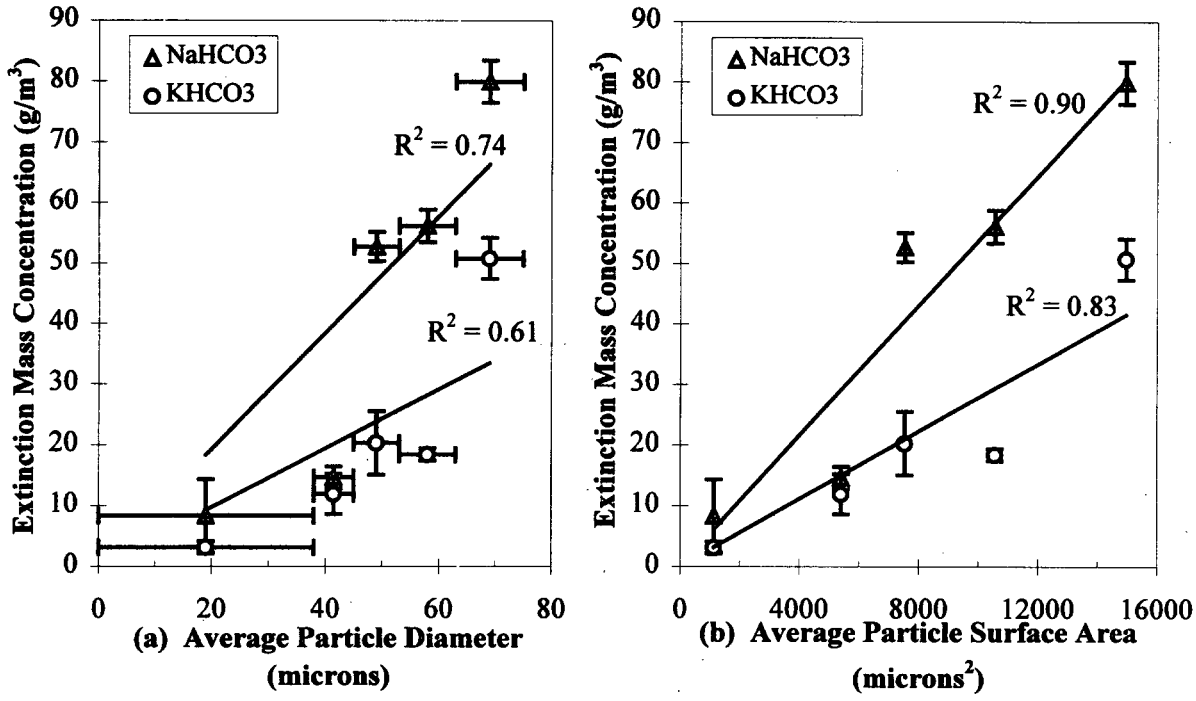

Figure 5: Extinction mass concentration as a function of (a) average particle diameter of the indicated size range and (b) average particle surface area, for a medium strain (310 s^{-1}) propane-air counterflow diffusion flame.

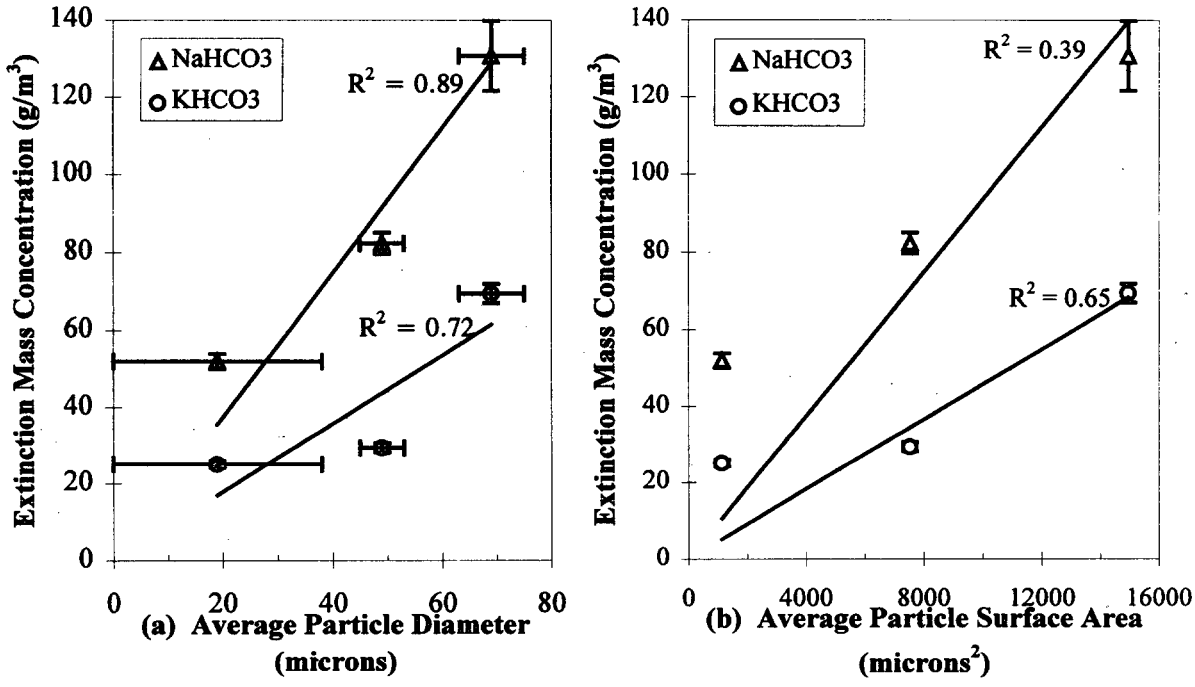

Figure 6: Extinction mass concentration as a function of (a) average particle diameter for the indicated size range and (b) average particle surface area, for an obscured n-heptane pan fire.

DEVELOPMENT OF A STANDARD CUP BURNER APPARATUS AND PROCEDURE

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ABSTRACT

The cup burner method has been utilized for many years to determine the starting point for full-scale verification testing and for the determination of the minimum extinguishing requirements for hazards involving Class B fuels. One of the historical weaknesses of the cup burner method has been the variability in the extinguishing values measured by different investigators, primarily due to the lack of a standardized cup burner apparatus and test methodology. We describe here the development of a standard cup burner apparatus and procedure as recently accepted by the ISO Task Group on Gaseous Media Fire Extinguishing Systems.

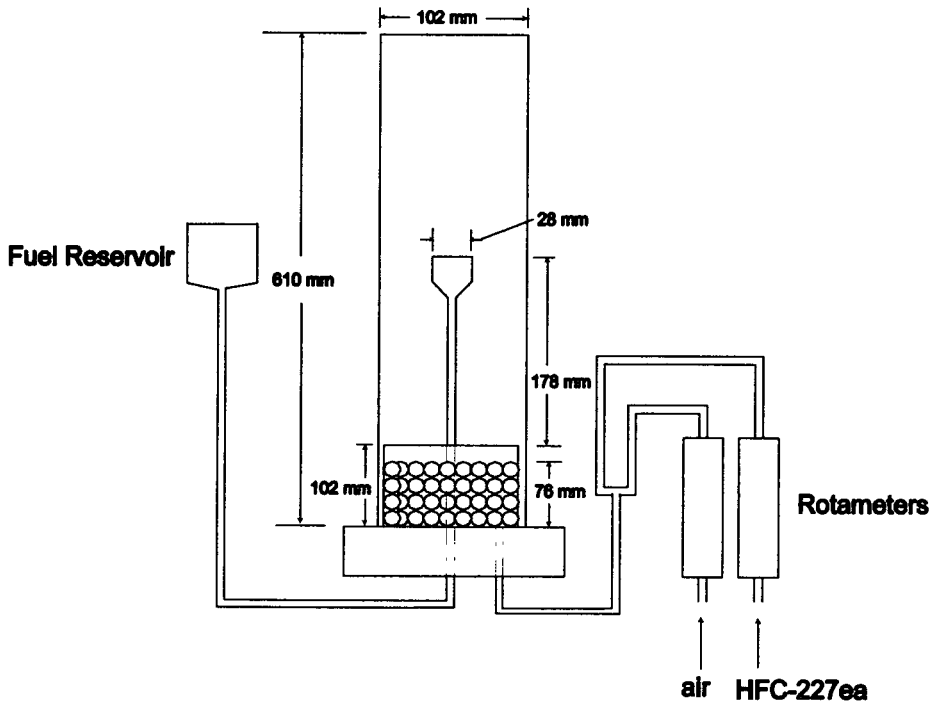
INTRODUCTION

In 1977, Hirst and Booth published their paper describing the development of the cup burner method, a laboratory-scale method for the determination of flame extinguishing concentrations of fire suppression agents [1].

A schematic diagram of the cup burner apparatus is shown in Figure 1. The inner cup is filled with a liquid fuel, the level of which is adjusted by means of a leveling device. In the case of a gaseous fuel, the cup can be packed with refractory materials. A mixture of air and suppression agent flows through a bed of glass beads and past the cup. A trial is conducted by adjusting the fuel level in the cup, and igniting the fuel. With the air flow held constant at a predetermined value and the liquid fuel level adjusted to the top of the cup, agent is gradually added to the air stream until the flame is extinguished. Air and agent flow rates are measured using calibrated rotameters, and the extinguishing concentration is calculated from the measured flowrates.

The great value of the cup burner method was that the cup burner flame proved to be more difficult to extinguish than full-scale fires of the same fuel, regardless of whether the fires were pool, spray, running, cluttered or obscured fires. As pointed out by Hirst and Booth, this built-in safety factor makes the cup burner method ideally suited for the measurement of flame-extinguishing concentrations for use in determining design concentrations.

Figure 1. Cup Burner Apparatus



Hirst and Booth attributed the greater stability of the cup burner flame to three causes:

1. An adequate supply of fresh air is always available to the flame.

2. The flame is undisturbed by movements of the fuel surface or irregularities in the airflow past the cup

3. The flame is anchored at its base by a partially premixed region, formed by the small eddy that results from the flow of air past the edge of the burner.

In recent years, numerous researchers have once again sought to employ the cup burner apparatus for the determination of the flame-extinguishing concentrations of Halon alternatives. However, many of these new agents were available only in experimental quantities, and as a result researchers constructed scaled-down versions of the original Hirst and Booth apparatus which require much less agent than the "full-scale" apparatus. Unfortunately, in many cases this was done without a clear understanding of the effects of scale on the measured extinguishing concentrations.

Creitz [2] in 1961 pointed out that the extinguishing concentration determined in a concentric tube burner was dependent upon the rate of fuel supply and the flow rate of air past the cup. Hirst and Booth [1] pointed out that the airflow past the edge of the cup forms an eddy which results in direct mixing of fuel vapor and air, and that the flame stability is strongly dependent upon this effect. In the cup burner apparatus the flame is anchored at its base by a partially premixed region formed by the small eddy that results from the flow of air past the edge of the burner. The relative velocity of the fuel vapor leaving the surface and the air flowing past the burner affects the composition of the premixed region, and hence the stability of the flame. As a result, Hirst and Booth took measures to eliminate any flow disturbances, specifying for example the use of a cup with a slowly increasing diameter and specifying the minimum height of the cup above the glass beads.

In addition to the requirement of maintaining an undisturbed air flow past the cup, researchers have established that numerous additional factors affect the extinguishing value obtained from the cup burner apparatus; these factors are summarized in Figure 2.

Figure 2. Variables Affecting Cup Burner Extinguishing Concentration

Chimney diameter, D
Cup diameter, d
Chimney to cup diameter ratio, D/d
Chimney length
Cup height above beads
Cup design
Disturbances in air flow past cup
Distance of fuel below top of cup (freeboard)
Linear velocity of air
Linear velocity of gaseous fuel
Temperature of fuel
Temperature of agent, air
Preburn time
Rate of agent increase in air stream
Oxygen content of air supply
Moisture content of air supply

The effect of scale on extinguishing concentrations measured in the cup burner apparatus has been reported by several investigators [3,4]. Table 1 shows the effect of varying the cup burner diameter on the measured result.

Table 1. Effect of Cup Diameter on Extinguishing Concentration
Fuel: n-Heptane; agent: HFC-227ea

Chimney OD (mm)	Cup OD (mm)	Extinguishing Concentration, % v/v
51	15	6.0
51	20	6.3
51	28	6.4

Based upon the large number of variables upon which the extinguishing concentration value depends on, the fire suppression industry has called for standardization of the cup burner method. The importance of obtaining reproducible values lies in the fact that current national and international fire suppression standards require that system design concentrations be based upon the cup burner extinguishing value plus a safety factor.

As a result, in January 1997 the ISO/TC 21/SC 8 Committee on Gaseous Media Fire Extinguishing Systems appointed a task group to develop a standard cup burner apparatus and procedure. At their meeting in May 1997, the Committee accepted the protocol produced by the task group. Major items related to the newly devised standard protocol include:

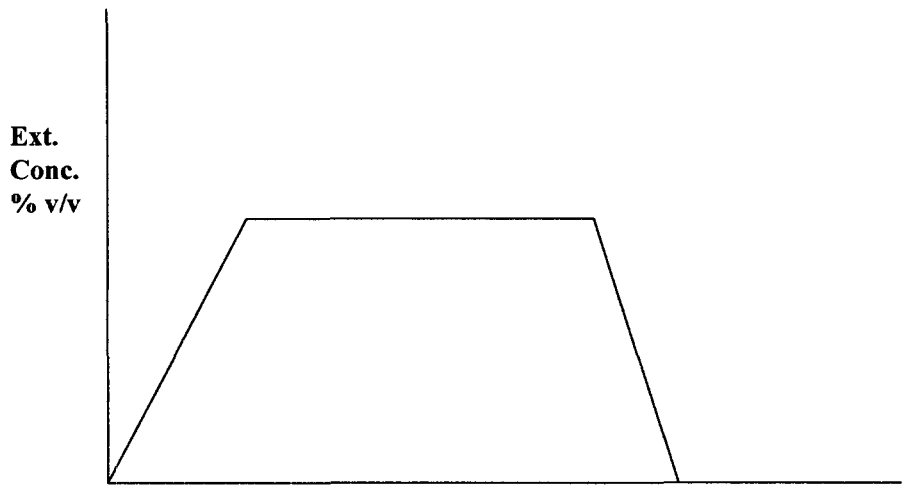
1. The rejection of all small-scale burners.

2. Determination of the variation of the extinguishing concentration with airflow.

3. Determination of extinguishing concentrations for heated fuels.

The new standard describes a single apparatus of well-defined dimensions. Because the extinguishing concentration is dependent upon the airflow, the new standard calls for the experimental determination of this dependence, rather than the common practice of setting the airflow to the arbitrary value of 40 L/min. Figure 3 shows the typical variation of the extinguishing concentration with airflow observed for halocarbon agents. Recent preliminary work at the University of Maryland [5] shows that for inert gases such as CO_2 at an airflow of 40 L/min the extinguishing concentration is still increasing with increased airflow, demonstrating the importance of measuring the dependence of the extinguishing concentration as a function of the airflow.

Figure 3. Dependence of the Extinguishing Concentration on Airflow



The standard also requires the determination of extinguishing concentrations for the case of elevated fuel temperatures. Measurements by NMERI [6] and VdS [7] have indicated that for halocarbon agents such as HFC-227ea, less agent is required for extinguishment at elevated fuel temperatures. However, it has been reported that for inert gas agents higher concentrations are required for extinguishment at elevated fuel temperatures [7].

The laboratory-to-laboratory reproducibility attainable employing the new standard can be seen from Table 2, which compares the results of several laboratories employing large-scale cup burners. As can be seen from Table 2, the agreement between different laboratories is excellent.

CONCLUSION

A new standard method and procedure for the cup burner apparatus has been developed and approved by the ISO/TC 21/SC 8 Committee on Gaseous Media Fire Extinguishing Systems. The laboratory-to-laboratory reproducibility attainable employing the new standard has been found to be excellent.

Table 2; Large-Scale Cup Burner Results
n-heptane fuel; HFC-227ea

Investigator	Chimney diameter, mm	Cup diameter, mm	Air Velocity, cm/s	Air Flow, L/min	Ext. Conc., % v/v
NRL	105	28	4.1	20	6.6
GLCC	102	28	5.1	25	6.7
FRIJ (metal)	85	30	11.7	40	6.5
FRIJ (glass)	85	30	11.7	40	6.6
Fenwal	85	28	11.7	40	6.6
VdS	85	28	11.7	40	6.6
U Maryland	85	28	11.7	40	6.7

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1997 INTERNATIONAL CONFERENCE ON OZONE PROTECTION TECHNOLOGIES

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PAPER: "The Economic Viability of Alternatives to Methyl Bromide"

PRESENTER: Dr Robert Van Slooten

Biography: Dr Robert Van Slooten is a Co-chair of the Economic Options Committee (EOC) of the UNEP Technology and Economic Assessment Panel (TEAP) under the Montreal Protocol on Substances That Deplete the Ozone Layer.

Following Lectureships in the Universities of Wales and Bristol, he served for 25 years as a member of the United Kingdom Government Economic Service in several . Departments of State in London and as Head of the Central Economic Service in the Northern Ireland Civil Service in Belfast. He was responsible for economic advice on environmental issues, including the Montreal Protocol, within the Department of Trade and Industry from 1989 to 1996. Following nomination by the U.K. Government in 1990, Dr Van Slooten has served as a Co-chair of the EOC and member of TEAP since 1991. Following the award of the Degree of Bachelor of Arts from Colgate University (1962), Dr Van Slooten was awarded the Degree of Doctor of Philosophy in Quantitative Economics from Iowa State University (1968). He holds dual U.S.A. and U.K. nationality. Since April 1996, Dr Van Slooten serves as an independent economic consultant focusing on issues affecting the interface between industry and the environment.

ECONOMIC OPTIONS COMMITTEE

REPORT OF THE METHYL BROMIDE TASK FORCE

1997 ASSESSMENT OF THE ECONOMIC VIABILITY OF ALTERNATIVES TO METHYL BROMIDE

APRIL 1997

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1997 ASSESSMENT OF THE ECONOMIC VIABILITY OF METHYL BROMIDE ALTERNATIVES

EXECUTIVE SUMMARY

1 INTRODUCTION

1.1 Decision VII/8 of the Parties requested the UNEP Technology and Economic Assessment Panel (TEAP) to prepare a report to the 9th Meeting of the Parties to enable the Parties to consider further adjustment to the control measures of methyl bromide. In undertaking this task, TEAP was required to address the availability of alternatives to methyl bromide for specific applications. The TEAP instructed its Economic Options Committee to provide information on the economic viability of alternatives to methyl bromide (TEAP Report, June 1996, p. 116).

1.2 Information on the uses of methyl bromide was reviewed to identify those which were likely to be associated with the more significant positive and negative economic impacts of phasing out methyl bromide. The information also shows where alternatives are already in use which helps to put the issue of substitution into perspective with respect to different countries and products.

1.3 The Task Force focussed on alternatives that are beyond the experimental stage and already in use. As soil fumigation is by far the largest and fastest growing use of methyl bromide, the Task Force gave most of its attention to this use. The quantities of methyl bromide used in post-harvest treatment and for treatment of structures are much smaller, but can have large economic value and therefore these uses were also addressed, but to a lesser degree, by the Task Force. Quarantine and pre-shipment uses are currently exempt from the control schedules of the Montreal Protocol and, therefore, are not addressed in this report.

1.4 External costs, which include environmental effects and human health effects, were addressed, at least qualitatively, in several of the studies reviewed by the Task Force. The Task Force itself was not able to deal directly with the issue of the external costs of methyl bromide alternatives. However, the Task Force recognised that these costs are important and that a close appreciation of their significance is needed to make informed decisions regarding the economics ofmethyl bromide and alternatives.

1.5 The Task Force used the information resources available to it particularly the 1997 MBTOC report to TEAP and the 1994 Assessment, the expertise of MBTOC members, and relied on the collective professional experience and judgement of the its members.

relied on the collective professional experience and judgement of the its members. Microeconomic evaluations of the economics of specific alternatives were carried out and a sector model approach was used to assess the wider economic impacts of switching to methyl bromide alternatives.

2 CONCLUSIONS

2.1 General Conclusions

2.1.1 **Progress with alternatives.** Where alternatives have been adopted, users have become more efficient as they develop expertise. This learning process is typical when different technologies are introduced. In the case of crop production, yield outcomes become more favourable over time. There are two general reasons for this improvement in the performance of alternatives. First, the technologies themselves improve. That is, incremental improvements take place in aspects such as materials, equipment and application rates (in the case of chemicals). Second, the human agents using the alternatives become more knowledgeable and skillfull over time. For example, they may better determine the optimal timing for certain tasks or become more adept at operating new equipment. Over time, these advances have been yield gaps between the alternatives and methyl bromide, and there are examples where yield exceeds that with methyl bromide use.

2.1.2 **Technology transfer.** The Task Force considered the potential for technology transfer between countries. Some technologies appear to be readily transferable, while others are constrained by factors such as climate (e.g., solarization), regulation (e.g., pesticide registration requirements), and the knowledge and skills of agricultural workers (e.g., integrated pest management systems). Efforts to increase relevant human capital (e.g., by training agricultural workers) could speed up the transfer and adoption of alternatives. Alternatives are being developed in many places with technology transfer originating from both developed and developing countries.

2.1.3 **Dangers of generalisation.** The costs of alternatives and methyl bromide will differ over time by crop, over time, and by location. Therefore, one must be careful not to generalise about the economic superiority of specific chemical alternatives, or between chemical and non-chemical technologies.

2.1.4 **Technical data.** On reviewing available information, the Task Force concluded that the technical and other information required for more comprehensive and rigorous assessments of the relative economic performance were not yet available for specific situations for many methyl bromide alternatives, whilst recognising that ongoing work in many institutions is already making good progress in generating the necessary skills, technical data and other information required for further work.

2.1.5 **Production systems.** Whilst most of the work undertaken in this assessment addressed the relative economic performance of specific methyl bromide alternatives, the Task Force recognised the advantages of adopting an approach based on identifiable production systems possibly involving combinations of specific alternatives and techniques that might be used if further work on the economic viability of alternatives requested.

2.2 Conclusions of the Microeconomic Evaluation: Soil Fumigation

2.2.1 **Dazomet.** The Task Force concluded, with input from MBTOC experts, that crop yields might initially decline by up to 10%. However, this yield loss can be overcome within 3 to 4 years as farmers become more familiar with the use of dazomet leading to improved application techniques. However, farmers may need assistance with the substitution process in the form of extension services, advice, and short term financial assistance.

2.2.2 **Dichloropropene (1,3 D or Telone) and chloropicrin.** The main findings are that (1) the product per unit costs are substantially more expensive than those for methyl bromide; (2) additional costs are incurred to modify equipment to enable implementation of these alternatives; and (3) on the basis of the data available to the Task Force yields are consistently lower with substantial variation in percentage decreases depending on the alternative used and the crop.

2.2.3 **Metam sodium.** The differences in production costs for metam soldium with respect to methyl bromide are quite varied. They range from +$1700/ha to +$800/ha in Colombia for cut flowers (TEAP, 1995); +$350/ha for strawberries in South Africa (FOE, 1996), and very small differences in Florida (Spreen et al. 1995). The switch to metam sodium involves costs on equipment, but no estimates are available; (2) a higher risk of crop failure is associated with metam sodium than with methyl bromide, but no estimates of the cost implications are available; and (3) the impact on yields vary.

2.2.4` **Integrated pest management (IPM).** The studies reviewed on IPM systems report consistently lower production costs than those for methyl bromide. The costs for IPM were estimated by TEAP to be lower by $1900/ha, or 28% lower (TEAP, 1995); and other estimates were lower by 67% (FOE, 1996). The CSIRO (1995) study estimated only slightly lower costs per square meter using IPM with only one crop and somewhat less than double the cost for one crop when IPM is used to get two crops. Yields using IPM are similar to those using methyl bromide for a single crop, whereas for double cropping yields are about 75% higher for IPM. Profitability is also about 75% higher for IPM with double cropping. Apart from the CSIRO (1995) study, no quantitative impacts are cited for IPM yields although profitability is estimated to be higher in almost all cases.

2.2.5 **Soilless substrates.** The main findings were (1) the costs of substitution will depend on whether the technique is only used for seedlings, or for the full growing of the crop. The estimates are as follows: $108/ha in Zimbabwe for tobacco seedlings; and $609/ha in Zimbabwe for paprika seed trays (FOE, 1996); (2) yield impacts are small or positive in switching to this alternative and risks are quoted as consistent with methyl bromide (MBTOC, 1997); and (3) the Danish study (Gyldenkaerne et.al. 1997) for greenhouse grown tomatoes estimates an increase in profitability of $2 to $3 per square metre and the pay back periods for investments in the technology are 1.4 to 4 years.

2.2.6 The use of soilless substrate for seed trays appears to be an attractive alternative for tobacco and some other seedlings, and has been successfully applied in South Africa, the USA and Zimbabwe. This technology is used for several crops and in several countries. Its use for greenhouse tomatoes (Denmark) and for other high-value crops (e.g. strawberries in The Netherlands) is less easily transferable due to capital-intensity and the need to be able to sell in high price markets (e.g., winter tomatoes and strawberries).

2.2.7 **Solarization.** The experience with solarisation technology reported from countries with abundant sunshine is encouraging, including several examples of lower production costs than with methyl bromide. The main factors affecting its adoption are that solarisation can only be technically effective where there is sufficient sunshine, soil conditions are favourable, technical assistance is available to local growers; and where the costs of an increased unproductive period can be accommodated.

2.2.8 **Steam.** The main findings are (1) where steam is a high cost alternative to methyl bromide the evidence suggests that it is suitable only in special circumstances where the higher cost is justified by the economic value of the reduced contamination risk e.g., in mother plant beds; and (2) the development of cost-efficient and mobile steam generating equipment is encouraging further uses of steam as an alternative to methyl bromide.

2.2.9 **Reduction of methyl bromide use through virtually impermeable film (VIF).** Improved tarping materials and techniques can reduce application rates by 30% to 50% leading to reduced emissions. Reported implications for production costs vary from cost savings of $1400/ha to a cost increase of $400/ha. Those facing cost increases would have an additional incentive to seek cost saving through the adoption of alternatives to methyl bromide.

2.3 Conclusions on Microeconomic Evaluation of Alternatives: Treatment of Post-Harvest Commodities and Structures

2.3.1 Use of heat and phosphine and carbon dioxide are prominent among the alternatives used for commodity and structural fumigation. The switch to an alternative may incur

additional one-off costs and treatment costs may also be higher or lower. The cost estimates are subject to various site-specific factors that make it difficult to provide estimates of general applicability.

2.4 Conclusions on Economic Viability of Alternatives: A Sector Approach

2.4.1 **Sector analyses.** Sector analyses highlight the dynamic nature of agricultural production and trade. Sector models can provide insight into marketing and distributional effects of changes in production systems that cannot be obtained through case studies or budget analyses. Existing patterns of production and trade depend, in part, on production costs associated with the use of methyl bromide. Switches to alternatives having different production costs, together with market forces and trade policies, can lead to forces that could change the location of crop production, trade patterns, consumer prices, jobs and foreign exchange earnings.

2.4.2 **The North American market for specialty winter fresh vegetables (e.g., tomatoes, melons, strawberries).** This market includes producers in the USA (Florida, Texas, California) and Mexico. It accounts for more than 20% of global methyl bromide use for soil fumigation i.e., about 16% of total global methyl bromide use. Using a sector model based on information available in 1994 (Spreen et al., 1995), the authors concluded that a rapid phaseout of methyl bromide, given alternatives available at that time, would impose annual economic costs on Florida of $623 million in shipping point revenues and a total cost of $1.0 billion. These estimates were substantially reduced in a re-run of the model using information on alternatives as of February 1997; shipping point revenues were reduced to $300 million.

2.4.3 **The European and North African regional market for winter fresh fruits and vegetables.** As in the North American market, there has been substantial concern about the potential migration of production to North Africa due to phasing out methyl bromide in the European Union. In principle, the same type of sector analysis as reported for the North America market is also applicable to this market. However, no model of this type is available for the European Union and North African market at present, although simpler quantitative models have been applied to Spain, France and Italy (Bonte, 1996). The results, based on alternatives available as of 1995, suggest economic losses for Spain, France and Italy and increased imports of selected fresh fruits and vegetables, probably from North Africa. Updated results are not available at this time. However, progress with alternatives and their application is likely to lower costs over time in ways that closely reflect the estimates reported for the North American market.

3 PRIORITIES FOR FURTHER WORK

3.1 Technical Data for Agricultural Production Systems. Assessments of the economics of alternatives depend on adequate technical data and other information that must be generated by the experimental work and field testing carried out by agricultural production scientists e.g., estimates of changes in crop yields, production costs, and the risks of crop failure for specific agricultural production systems in specific locations. Technical data on production systems and human capital inputs for IPM systems, whether chemical-free or not, would be of particular interest.

3.2 External Costs. Assessments of alternatives to methyl bromide should include information on economic costs which are not internalised by market prices but are associated with agricultural production and marketing e.g., the effects of toxicity of methyl bromide or alternatives on human health. The Task Force could not address the issue of external costs in this report due to time and resource constraints. However, in further work on assessing the relative economics of methyl bromide and alternatives, the external cost issue should be given high priority.

3.3 Quantitative Estimation of the Economic Viability of Alternatives. The application of quantitative methods to assessments of the relative economics of methyl bromide and alternatives is both important and practicable. The North American model of the winter fresh vegetable maket involving the USA, Mexico and Canada demonstrates the value of this approach and the potential for developing further applications to improve (1) assessments of the economic viability of alternatives and (2) estimates of the costs and benefits of phasing out methyl bromide in Article 5(1) countries.

Mobile Air Conditioning Service Industry Field Experience with Alternate Refrigerants

International Conference on Ozone Protection Technologies
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Simon. Oulouhojian, President MACS Ward Atkinson, MACS Technical Advisor

International Needs

Automotive A/C Requirements

When the Montreal Protocol was signed, CFCs were no longer used as an aerosol in the U.S. and the mobile A/C industry was consuming the greatest amount of CFCs in the world. Since CFCs were low in cost and not considered as a problem, normal A/C service included venting the entire charge.

U.S. Clean Air Act

It became obvious that to comply with the U.S. Clean Air Act and allow the consumer the use of their A/C systems, the use of CFC-12 when servicing mobile A/C systems had to be dramatically revised.

EPA Action

Through efforts of the automobile manufacturers, service industry and the EPA, a field study was done in 1988 to determine if CFC-12 used in the mobile A/C systems could be reused.

After considerable effort the auto industry concluded in January 1989 that CFC-12 could be reused and met the requirements for continued A/C system warranties.

SAE Documents

In February 1992, the EPA requested the SAE Interior Climate Control Committee to establish engineering documents for the smooth transition from CFC-12 to a non-ozone depleting refrigerant substitute.

After considerable auto industry effort, including that of refrigerant manufacture's, equipment manufacture's and the service sector, the SAE documents were completed and sent to the EPA. More than 20 documents addressing the CFC transition issue, including recovery and on-site cleaning of CFC-12 for reuse was published. Additional documents provide technician service procedures for reducing the emission of refrigerant during service of the A/C systems. These SAE documents are a series of engineering guidelines that address minimum requirements for any alternate refrigerant being considered for use in automotive A/C systems. These requirements include mobile A/C system material and lubricant compatibility, refrigerant stability, and A/C system performance.

As had been requested by the EPA, in April 1994 these SAE documents were transmitted to the EPA Administrator Carol Browner.

SNAP Rule

The EPA SNAP rule covers many substances considered ozone depleting. One section of the rule addresses the refrigerant used in automotive A/C systems.

As the industry moved away from CFC-12 and the price increased, many alternate refrigerants began to appear in the service sector. The SNAP rule was misinterpreted by many merchandisers of these alternate refrigerants, and until action by the EPA stopping the use of the term "drop in," considerable service industry problems had occurred. Even today the field and consumers are still misinformed and unaware of the requirements when using an alternate refrigerant for automotive use.

Unfortunately, the EPA did not use the SAE alternate refrigerant engineering documents that they had requested to screen all alternate refrigerants. If the EPA had required that refrigerants being considered under the SNAP requirements must meet these SAE requirements, some current field problems may not exist. The only areas that the EPA reviewed for alternate refrigerants were environmental and safety concerns.

Except for R134a none of the SNAP listed refrigerants have attempted to meet all the SAE alternate refrigerant criteria. Until this information is provided, by each refrigerant supplier, the consumer becomes the testing source. It is very difficult to assure that an alternate refrigerant will meet the requirements of the hundreds of different mobile A/C system designs that are currently in the field. The auto A/C system manufacturers spent considerable money and effort to establish the R134a retrofit requirements for their systems. It is impossible for the supplier of another alternate refrigerant to provide the same level of customer assurance for their product on every type of vehicle A/C system in the marketplace.

Industry Action

Auto Industry Response

The auto industry decided that HFC-134a was the only refrigerant that would meet their need for new vehicle applications. The industry conversion to use R134a started in the 1992

model year. With the revised earlier phaseout of CFCs, accelerated engineering activity to determine the best way to address the future servicing of the existing CFC-12 fleet was required. Since HFC-134a had been selected for new vehicles, it became the candidate for retrofitting the R12 fleet. However, at the same time other refrigerants were being considered, including a blend from one refrigerant supplier, for retrofitting the R12 fleet. As some retrofitting complexities became obvious, including concerns with the blend refrigerant, R134a became the best choice. There was also concern that with the additional equipment cost required for a third refrigerant, the use of R134a for both new and retrofitted A/C systems seemed obvious.

MACS Petitions

MACS petitioned the EPA pointing out significant concerns, regarding alternate refrigerants and reclaiming refrigerants, that would cause problems both in the mobile and commercial service industries.

Service Fittings and Labels

On May 19, 1993, the Mobile Air Conditioning Society submitted a petition to the Environmental Protection Agency (EPA), requesting that EPA take several actions to protect the consumers and the mobile air-conditioning industry. MACS expressed concern that non-standardized fittings and labeling of retrofitted automotive air-conditioning systems would permit the accidental charging of air-conditioning systems with the wrong refrigerants. This petition was not acted upon by EPA until such time that many SNAP listed refrigerants had already entered the service market. Even today, with the federal requirement, there is minimal enforcement in the field and alternate refrigerants are being installed in mobile A/C systems without the refrigerant-specific service equipment and vehicle service fittings.

Reclaimed Refrigerant Labeling

Also, a petition filed by MACS in July 1995 addressed the issue of refrigerant purity. Since there are no federal requirements that a container must have any identification as to the product purity, it was felt that a form of identification was required. This was not a concern with a product sold by recognized refrigerant manufacturers. In 1994, refrigerant containers that had been repainted and relabeled as R12, but in fact contained R22, were seen in the field. The recent counterfeiting of CFC-12 using a major refrigerant manufacturers' identification has added to the contamination of mobile A/C systems.

Under the U.S. Clean Air Act, used refrigerant can be imported and sold without any requirements that it meet a purity level or be labeled as to its content.

At the same time, any reclaimer in the business of buying and selling used refrigerant is not required to label the product being sold to indicate its purity or whether it is new or reclaimed. Although it is the intent to have clean refrigerant, there are inadequate federal Clean Air Act requirements that all the refrigerants processed by the reclaimer meet the ARI reclaimed refrigerant purity requirements.

Service Sector Action

Technician Certification

The Mobile Air Conditioning Society as only one source has provided certification for more than 450,000 technicians. MACS has endeavored through this program to alert the technician of these potential servicing problems. It is estimated that more than a million technicians have been included in this EPA mandatory technician certification program. With this extensive number of service technicians, it is impossible to keep them informed of technical information and changing federal requirements.

Equipment

Refrigerant recovery/recycling equipment was developed by many manufactures to meet the SAE requirements identified in the federal Clean Air Act. These requirements cover the recovery and on-site recycling for reuse of both CFC-12 and HFC-134a refrigerants.

Unlike R12 and R134a, currently there are no federal or industry standards for the handling of other alternate refrigerants listed under the SNAP rules.

From existing information it may not be possible to recover/recycle blend refrigerants on site for direct reuse. Since the blend refrigerants contain class II substances, they cannot be vented. If the technologies cannot be developed to handle on-site, reformulation and recycling, of blend refrigerants then the only choice will be to recover and send the refrigerant off-site. This means that there is added expense since the refrigerant must be transported to the original supplier or reclaimer for salvage or destruction. This transportation and processing of this used refrigerant results in the consumption of more energy and emissions to the environment.

Current Industry Status

Supply and Cost of R12

In order to meet the future needs of their CFC-12 customers, many of the auto manufacturer's stockpiled refrigerant. Adequate supplies of CFC-12 refrigerant were available to service the CFC-12 feet in 1996 and 1997. However, in early 1996, speculation of the impending shortage of CFC-12 drove the price to a critical cost plateau, prematurely curtailing it use.The CFC-12 cost remained at this high level until the demand had subsided for the service season. Early in 1997 the price again rose to the 1996 level. By mid 1997, sales of CFC-12 were greatly

reduced and increased retrofitting of CFC-12 systems was taking place, using the lower cost R134a and other alternate blend refrigerants.

This price information reflects the market price paid by a large quantity purchaser. It does not indicate the single container prices reported to be in the over 800-dollar range.

Retrofit Activity

With the auto industry converting to HFC-134a and the expected production phase-out of new CFC-12, it was originally projected that an estimated 40 million CFC-12 A/C vehicles would require retrofitting. In 1995, it was estimated that the U.S. CFC-12 fleet was just more than 100 million vehicles. To provide a smooth transition, it was originally projected that retrofitting would grow at a low rate starting in 1994 and the operational CFC-12 vehicles would be phased out by the year 2002.

In order to achieve this retrofit level, it was estimated that in 1994 and 1995 about 3 million vehicles should have been annually retrofitted. By 1997 and 1998 the annual retrofitting level would have been in the 7.5 million range. Unfortunately, retrofitting of the CFC-12 fleet did not materialize until the price of CFC-12 took a dramatic jump.

In 1994, the cost of CFC-12 was in the eight dollar a pound range with R134a being in the six dollar a pound range. The R12 cost escalated to more than eighteen dollars per pound in 1996. However, in 1997 with the high cost of R12 the price of R134a had decreased to the $2.50 per pound range, which resulted in more R12 vehicles being retrofitted.

Also, with the high cost of R12, the use of alternate refrigerants became more evident in the service industry in 1997. When comparing the alternate blend refrigerants, their street costs per pound are between the low seven and ten dollar ranges. However, R134a has the lowest cost, being in the $2.50 per pound range.

At the same time, the sale and use of flammable refrigerants in mobile A/C systems continued both in the U. S. and Canada.

Contamination

With the lack of the initial implementation and enforcement by the EPA requiring unique refrigerant fittings and labels, alternate refrigerants were sold and directly used in CFC-12 mobile A/C systems. Even today, with the thousands of service facilities across the country, it is impossible to have adequate enforcement assuring compliance with the fitting and label requirements.

In addition, during the 1997 service season, R134a could be purchased by the general public in any container size. With R134a costing 80% less than R12 and being readily available to uncertified people, it can easily be used to service A/C systems.

Alternate Refrigerants

The use of alternate blend refrigerants that contain R22 has resulted in damage to seals, O-rings and hose material in mobile A/C systems and service equipment. These problems have been in many cases "silent failures", since they did not exhibit any external damage. Typical failures resulted in mechanical destruction of the material causing system refrigerant leaks or plugging of the refrigerant circuit. Typically, the system experienced compressor failures.

Although the EPA SNAP requirements include the replacement of refrigerant hoses on mobile A/C systems that do not have barrier hoses there are no assurances that other polymer material failures within the system will not occur.

Unlike commercial refrigeration systems that are of a rigid pipe construction, mobile A/C systems use polymers throughout the system. This material is used for sealing at refrigerant fittings and the flexible hoses used to transmit the refrigerant. Since the mobile A/C system manufacturers have only produced systems that use R12 or R134a the effect of other refrigerants on these polymers is generally unknown. SAE and commercial refrigerant documents identify test procedures to determine material compatibility with a refrigerant. Refrigerant that is not compatible with the materials traditionally found in the mobile A/C system failure's result in the release of the refrigerant.

Enforcement

As the cost of R12 increased the service sector was flooded with other refrigerants that mobile A/C systems had not been designed to use. The sale and use of flammable refrigerants also occurred in the marketplace. Even thought federal law prohibits the use of flammable refrigerant in CFC-12 systems, new promotions and activities by the promoters, flammable refrigerants are being used to service automotive A/C systems.

It is estimated that nearly 20 million A/C vehicles are serviced annually by millions of people, some qualified, and some simply doing it themselves. With this potential magnitude of people servicing mobile A/C systems, it is impossible to provide factual information to them. Therefore the best sales person on the street will gain their confidence, even if the refrigerant they are selling is illegal, a safety concern, or may cause system operating problems.

With this broad sector of service activity it is impossible to provide correct information, let alone have any form of enforcement.

One example was the convincing of a major East coast city purchasing agent that a blend refrigerant was a direct replacement for CFC-12. It was purchased and used in the city's motor vehicle fleet. The result was a blend refrigerant, without the required unique container fitting, was directly installed in vehicle A/C systems. The use of this refrigerant resulted in damage to the city owned vehicles and their service shop equipment. The enforcement was after the fact, which did not prevent the initial costly problem.

The use of other refrigerants is an ongoing problem in thousands of shops across the country, including new car dealerships. This is in spite of the fact that the auto manufacturers have sent numerous notifications that they should only use CFC-12 and HFC-134a.

MACS Worldwide membership numbers 1,500 service facilities across the country and can only place a small dent in the vast service sector in getting the information to the A/C service technician.

Reclaimed Refrigerant

Unfortunately, the refrigerant industry did not aggressively promote the creditable certification of reclaim facilities. Under the EPA requirements, it is easy for any person to obtain an EPA approval as a refrigerant reclaim facility. As part of the refrigerant industry activities, ARI established a facility certification program that provides an overview of each facility's reclaimed refrigerant quality. Under this program each facility is monitored, assuring that the processed refrigerant meets the ARI reclaimed purity requirements. Currently, the EPA has listed 66 facilities in the reclaim program. Of the EPA listed reclaimers, only 18 are in the ARI certification program.

An example of this unenforced program was documented when a chain of repair facilities purchased CFC-12 refrigerant, over an extended period of time, from one of the EPA, listed reclaimers. The refrigerant was sold as new but upon checking was found to contain other refrigerants, including R22. The practice by reclaim facilities of mixing polluted refrigerants with other refrigerant, hoping to dilute the contamination, has evidently been commonplace.

If the EPA reclaimed refrigerant program requires that reclaimed refrigerant meet the ARI purity level limiting contamination to 0.05% specification, it is imperative that there be stronger enforcement. Without labeling requirements identifying container contents and purity, the use of reclaimed refrigerant can result in system failures.

The auto industry has refrigerant identification available that can determine if the A/C system or refrigerant container contains R12 or R134a. However, the identifier cannot identify the presence of other impurities such as acids. If the reclaimed refrigerant should contain acids from a commercial compressor burnout, it can become devastating to the material used in mobile A/C systems.

Field Service Activities

- Since the service industry no longer vents refrigerant during service and many refrigerants, both legal and illegal, have entered the service industry, contamination can occur in many forms.

- It is generally felt that any A/C refrigerant contamination level in excess 2% to 3% by weight will affect the operation of the mobile A/C system. It is therefore important that the technician identify the system's refrigerant purity before starting to service it.

- As the field has reported often, by not identifying the refrigerant before using recovery equipment, they have had costly contamination problems of their equipment and vehicles.

- The problems resulting from refrigerant contamination can include internal compressor failures, clutch failures and failure of hose O-ring and seal material. These same problems can also occur in recovery/recycling equipment.

- There is also reduced A/C system performance caused by improper refrigerant control settings and excessive system operating pressures.

In addition, not considering the effect of a shop's recover/recycling equipment being contaminated will unknowingly spread the refrigerant to other A/C systems and cause problems.

- In the case of flammable refrigerants, there are field reports of vehicle fires and individuals being burned.

- Unfortunately, the mobile A/C industry even with the best initial efforts for a smooth transition from CFCs, is currently plagued with many problems. It is expected that, as time prevails, these problems will be diminished. However, in the meantime, these problems increase the repair costs for the consumer as both CFC-12 and HFC-134a A/C systems become contaminated.

Alternatives for CFC-12 Refrigerant in Automotive Air Conditioning

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Abstract

Ten refrigerants including CFC-12, HFC-134a, and eight refrigerant blends were tested in an instrumented automotive air-conditioning system designed for CFC-12. The refrigerants were compared at three test conditions for refrigeration capacity, coefficient of performance, compressor discharge pressure, compressor discharge temperature, and evaporator outlet pressure. Due to limitations of the testing, test results should not be used as conclusive evidence of the performance of refrigerants. However, the results were obtained by testing all the refrigerants in the same system under the same conditions, and the results provide an indication of the comparative performance of the refrigerants. Refrigeration capacities for CFC-12 substitutes ranged from 9 percent lower to 9 percent higher than capacities for CFC-12. Capacities for refrigerant blends containing HCFC-22 tended to be higher than capacities for CFC-12 and other substitutes for CFC-12. Evaporating pressures for HFC-134a closely matched those for CFC-12. Compressor discharge pressures for HFC-134a ranged from 4 to 8 percent higher than those for CFC-12. Compressor discharge pressures for refrigerant blends containing HCFC-22 were 17 to 34 percent higher than those for CFC-12. Discharge temperatures for two of the four blends that contained HCFC-22 were more than 5C° higher than temperatures for CFC-12. Further laboratory and field testing would be required to adequately evaluate performance and other important refrigerant characteristics including materials compatibility, chemical stability, fractionation, and long-term durability.

Introduction

Title VI of the 1990 Clean Air Act Amendments requires the U.S. EPA (Environmental Protection Agency) to regulate substitutes for ozone depleting substances, including CFC (chlorofluorocarbon)-12 [1]. Title VI, Section 612 mandates "that it shall be unlawful to replace any class I or class II [ozone-depleting] substance with any substitute substance which the [EPA] Administrator determines may present adverse effects to human health or the environment.... The Administrator shall publish a list of (A) the substitutes prohibited under this subsection for specific uses and (B) the safe alternatives identified under this subsection for specific uses."

EPA implemented the Title VI, Section 612 requirements with the SNAP (Significant New Alternatives Policy) Program in 1994[2]. Under the SNAP Program, EPA evaluates substitutes for effects on human health or the environment including toxicity, flammability, ozone depletion, and global warming. Under the SNAP Program, EPA does not evaluate performance characteristics such as refrigeration capacity, efficiency, materials compatibility, miscibility with lubricants, and thermodynamic properties. As of June 3, 1997, 10 substitutes for CFC-12 in motor vehicle air conditioning were listed as "acceptable subject to use conditions." Use conditions include a requirement for unique fittings to prevent cross-contamination, a requirement for labeling to identify refrigerants in each vehicle, a prohibition against topping off one refrigerant with another, and a prohibition against recycling of refrigerant blends. Additionally, refrigerant blends containing HCFC (hydrochlorofluorocarbon)-22 require the use of barrier hoses to reduce permeation.

The substitutes listed as acceptable subject to use conditions under the SNAP Program include HFC (hydrofluorocarbon)-134a, three refrigerant blends containing HFC-134a, five blends containing HCFC-22, and a blend with a composition claimed as confidential business information by the manufacturer. Compositions of nine substitute refrigerants that were tested for performance are shown in Table 1. Since the testing was completed, another blend called GHG-X5 (0.41 HCFC-22 / 0.15 HCFC-142b / 0.04 isobutane / 0.40 HFC-227ea) has been listed as acceptable under the SNAP program. Only pure HFC-134a has been endorsed as a substitute for CFC-12 by the automotive OEMs (original equipment manufacturers). However, many of the refrigerant blends are currently available or will be available in the U.S. market.

EPA's National Risk Management Research Laboratory performed the testing described in this paper to provide information to EPA's regulatory office and the automotive air-conditioning industry. Testing was conducted at the Air Pollution Prevention and Control Division located in Research Triangle Park, North Carolina. This EPA laboratory has had prior experience in testing automotive air-conditioning systems and refrigerants[3,4,5].

Table 1. Refrigerant Composition (Percent by Weight)

Name	HCFC-22	HCFC-124	HCFC-142b	HFC-134a	Butane (R-600)	Iso-butane (R-600a)	Propri-etary lubricant
HFC-134a				100			
R-406A/GHG/McCool	55		41			4	
GHG-X4/Autofrost/Chill-It	51	28.5	16.5			4	
GHG-HP	65		31			4	
Hot Shot/Kar Kool	50	39	9.5			1.5	
FREEZE 12			20	80			
FRIGC FR-12		39		59	2		
Free Zone/RB-276			19	79			2
Ikon-12	Composition claimed as confidential business information						

Description of Testing

Refrigerants were tested in an instrumented, OEM, automotive air-conditioning system designed for CFC-12. The 1993 passenger car system had an orifice tube expansion device and a suction line accumulator. The evaporator and housing were located inside an insulated calorimeter chamber. Refrigeration capacity was determined by measuring the power input to electric heaters, heater fans, and evaporator fan inside the chamber. The capacity was determined with an uncertainty of approximately ±100W and a repeatability of ±30W. COP (coefficient of performance) was determined from the measured power input to the compressor with an uncertainty of approximately ±75W and a repeatability of ±50W. Pressures were measured with capacitive pressure transducers with an uncertainty of ±0.1 psia (±0.7 kPa) for 0-100 psia (0-689 kPa) and ±0.6 psia (±4.1 kPa) for 100-250 psia (689-1724 kPa). Refrigerant temperatures were measured with an uncertainty of ±0.9 F° (0.5 C°) with thermocouple probes inserted into the fluid. Instrumentation was similar to that described in a previous paper[3].

A new compressor was broken in for 40 hours with CFC-12 refrigerant and mineral oil lubricant. Following the break-in period, baseline tests were performed with CFC-12 and mineral oil.

Refrigerant blends were mixed in the laboratory using an electronic scale with an accuracy of ±0.2 gram. The Free Zone/RB-276 blend was not mixed in the laboratory because it contains a proprietary lubricant. A 30-pound (13.6 kg) cylinder of the Free Zone/RB-276 was obtained and the blend was charged into the system as a liquid from the cylinder. For all the refrigerant blends, manufacturer or supplier recommendations on charging the system were followed if they were available. Before each refrigerant was charged, the system was triple-flushed with dry nitrogen and evacuated until the system held a vacuum of less than 25 μm Hg for 15 minutes to ensure that no significant amount of residual refrigerant or moisture remained in the system. For all tests, minimal superheat at the compressor inlet indicated the presence of some saturated liquid in the suction line accumulator and confirmed that the system was fully charged.

Refrigerant manufacturer recommendations on lubricants were also followed if they were available. The four refrigerant blends that contained HCFC-22 were tested with the same mineral oil used with CFC-12. FREEZE 12 and FRIGC FR-12 were tested with 3 ounces (89 cm^3) of POE (polyolester) lubricant added to the existing mineral oil. The POE lubricant had a viscosity reported by the manufacturer to be 134 cSt at 40°C and 25 cSt at 100°C. Free Zone/RB-276, containing 2 percent of a proprietary lubricant, was tested with the mineral oil used with CFC-12. Ikon-12 was tested with a POE lubricant that had previously been tested for compatibility with the refrigerant[5]. HFC-134a was tested with PAG (polyalkylene glycol) lubricant added to the mineral oil used with CFC-12, as recommended by the OEM. When lubricants were changed, residual lubricant was removed from the system by repeatedly flushing with a solvent followed by evacuation to remove the solvent. The accumulator/drier was removed each time before the system was flushed and was replaced with a new unit after flushing. Heptane was used as a solvent to remove mineral oil and POE lubricant, and methanol was used to remove PAG lubricant. Solvents were not used to flush the compressor, but the compressor was repeatedly flushed with heated lubricant.

Conditions for the three tests performed with each refrigerant are shown in Table 2. Evaporator air inlet temperatures were set high enough to provide sufficient load to prevent cycling of the compressor. Steady-state operation enabled measurement and comparison of performance characteristics including refrigeration capacity, COP, pressures, and temperatures. Although a significant part of the refrigeration load on an air-conditioning system can result from moisture condensing on the surface of the evaporator, in the test system, air inside the evaporator chamber was not humidified to simplify the measurement of refrigeration capacity. Relative humidity was maintained at a low level during testing to prevent any condensation of water vapor. Electrical potential applied to the evaporator fan motor was regulated and maintained at 10.6VDC to obtain consistent air flow through the evaporator.

Table 2. Test Conditions

	1	2	3
Compressor rotational speed (rpm)	1000	2000	3000
Evaporator air inlet temperature, °C (°F)	37.8 (100)	43.3 (110)	48.9 (120)
Condenser air inlet temperature, °C (°F)	46.1 (115)	35.0 (95)	35.0 (95)
Condenser air inlet velocity, m/s (ft/min)	1.02 (200)	1.78 (350)	1.78 (350)
Compressor ambient temperature, °C (°F)	54.4 (130)	54.4 (130)	54.4 (130)

At each test condition, data were recorded at 30-minute intervals during a 2-hour period to ensure steady-state operation. After initial baseline tests with CFC-12 and tests with the nine substitutes were completed, tests were repeated with CFC-12 to ensure that system performance had not degraded during the course of the testing. Comparisons of the final tests with the initial CFC-12 tests are shown in Table 3. Refrigeration capacity remained within ±2 percent. At the 1000, 2000, and 3000 rpm test conditions, COP increased by 1.5, 5.4, and 3.9 percent, respectively. This increase in COP may have resulted, in part, from additional break-in of the compressor during the testing.

Table 3. Comparison of Final Tests with CFC-12 to Initial Baseline Tests With CFC-12

	1	2	3
Refrigeration capacity (percent change)	+1.0	-0.4	-2.0
COP (percent change)	+1.5	+5.4	+3.9

Limitations of Testing

Tests results described in this paper contribute to the information available in the open technical literature on alternative refrigerants. However, results should not be used as conclusive evidence of any refrigerant's relative merits for the following reasons:

1. All tests were performed with one automotive air-conditioning system. Performance may vary between different vehicle air-conditioning systems.

2. Only three tests were performed for each refrigerant. Automotive air conditioners operate over a greater range of conditions than represented by the test conditions.

3. Tests were performed under steady-state conditions. Automotive air conditioners usually operate under transient conditions with changing rotational speed, changing load conditions, changing capacity, or on/off cycling of the compressor.

4. In the laboratory, refrigerant blend composition was carefully controlled for the tests. In the field, composition can change due to leakage or fractionation during servicing. Performance may vary with changing blend composition.

5. Tests were performed to evaluate only air-conditioning system performance. Other important factors involved in refrigerant evaluation include materials compatibility, chemical stability, fractionation, and long-term durability. Extensive laboratory and field testing is required to adequately evaluate these factors.

Discussion of Results

Refrigeration capacities for the ten refrigerants are compared at the three test conditions in Figure 1. Of the ten refrigerants tested, HFC-134a had the lowest capacities with values ranging from 8 to 9 percent lower than the capacities for CFC-12. Capacities for the four blends that contained HCFC-22 were 0 to 9 percent higher than those for CFC-12 at the three test conditions. Capacities for the three blends that contained HFC-134a were 3 to 9 percent lower than those for CFC-12. Refrigeration capacities for Ikon-12 were 2 to 6 percent lower than those for CFC-12. Comparison of refrigeration capacities for Ikon-12 with those for HFC-134a is consistent with results obtained in a previous evaluation[5].

COPs are compared in Figure 2. COPs for HFC-134a ranged from 7 to 9 percent lower than those for CFC-12. COPs for HFC-134a and the four blends that contained HCFC-22 tended to be lower than the COPs for Ikon-12 and the three blends that contained HFC-134a. Comparison of the COPs for Ikon-12 with those for HFC-134a is consistent with results obtained in a previous evaluation[5].

Evaporator outlet pressures are compared in Figure 3. HFC-134a evaporator pressures most closely matched those of CFC-12 at the three test conditions. The four blends that contained HCFC-22 had evaporator pressures that were notably higher than the pressures for CFC-12. Ikon-12 and the three blends that contained HFC-134a had evaporator pressures that were lower than those for CFC-12.

Compressor discharge pressures are compared in Figure 4. Discharge pressures for HFC-134a were 4 to 8 percent higher than those for CFC-12. Compressor discharge pressures for the four blends that contained HCFC-22 were 17 to 34 percent higher than the pressures for CFC-12. The three blends that contained HFC-134a had discharge pressures that were lower than those for CFC-12.

Compressor discharge temperatures are compared in Figure 5. Discharge temperatures for HFC-134a and for two of the blends that contained HFC-134a were more than 5C° lower than temperatures for CFC-12. Discharge temperatures for two of the four blends that contained HCFC-22 were more than 5C° higher than temperatures for CFC-12.

Conclusions

Due to the limitations of testing, test results should not be used as conclusive evidence of the performance of refrigerants, as discussed above. However, the results do provide some useful indications of performance. Results from this evaluation indicated that the refrigeration capacities for all the refrigerants tested are likely to be adequate compared to the capacity for CFC-12. Although HFC-134a had the lowest capacity, its capacity was within 10 percent of that for CFC-12. The four refrigerant blends that contain HCFC-22 had the advantage of somewhat higher capacities than those of the other substitutes for CFC-12. Higher refrigeration capacity can improve occupant comfort during certain operating conditions when the refrigeration load is high compared to the available capacity.

However, the blends that contain HCFC-22 had the disadvantage of higher evaporating and condensing pressures. Higher pressures can increase the stress on air-conditioning system components and can have a negative effect on control systems with pressure sensing devices. Compressor discharge temperatures for two of the four blends that contained HCFC-22 were more than 5C° higher than temperatures for CFC-12. Higher discharge temperatures can cause the lubricant to break down at a faster rate and may cause a reduction of the time before failure of the system. Discharge temperatures for HFC-134a and for two of the blends that contained HFC-134a were more than 5C° lower than temperatures for CFC-12. Lower discharge temperatures may increase the durability of the system.

Results indicated that the COPs for all the refrigerants tested are likely to be adequate compared to the COP for CFC-12. Refrigerants with lower COPs may cause a slight increase in vehicle fuel consumption.

Ikon®-12 and the refrigerant blends that contain HFC-134a had the advantage of lower condensing pressures than those of HFC-134a. Ikon®-12 and the refrigerant blends that contain HFC-134a also had the advantage of slightly higher refrigeration capacities than those of HFC-134a. However, all zeotropic blends have the disadvantage of potential fractionation during installation, operation, and servicing. Performance may decline with changing blend composition. Pure HFC-134a has no fractionation and has had more extensive testing for materials compatibility and system durability.

Notice

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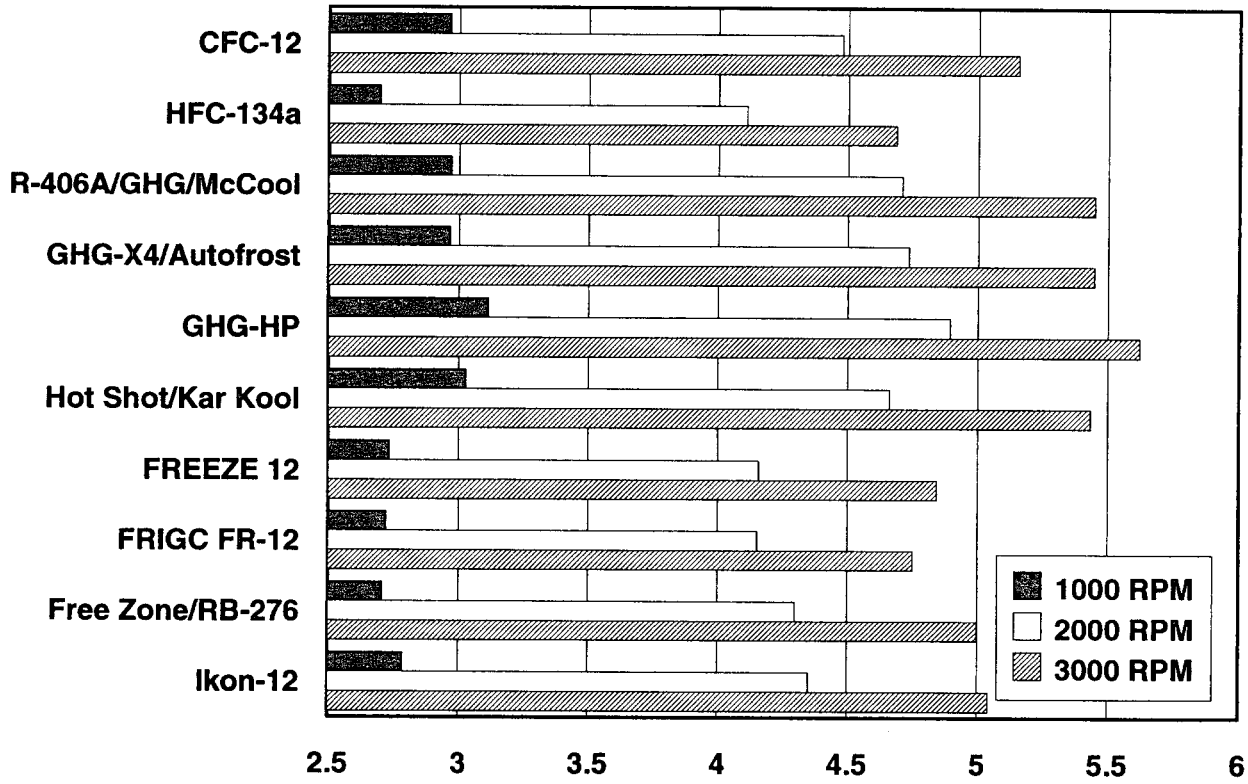

Figure 1. Refrigeration Capacity (kW)

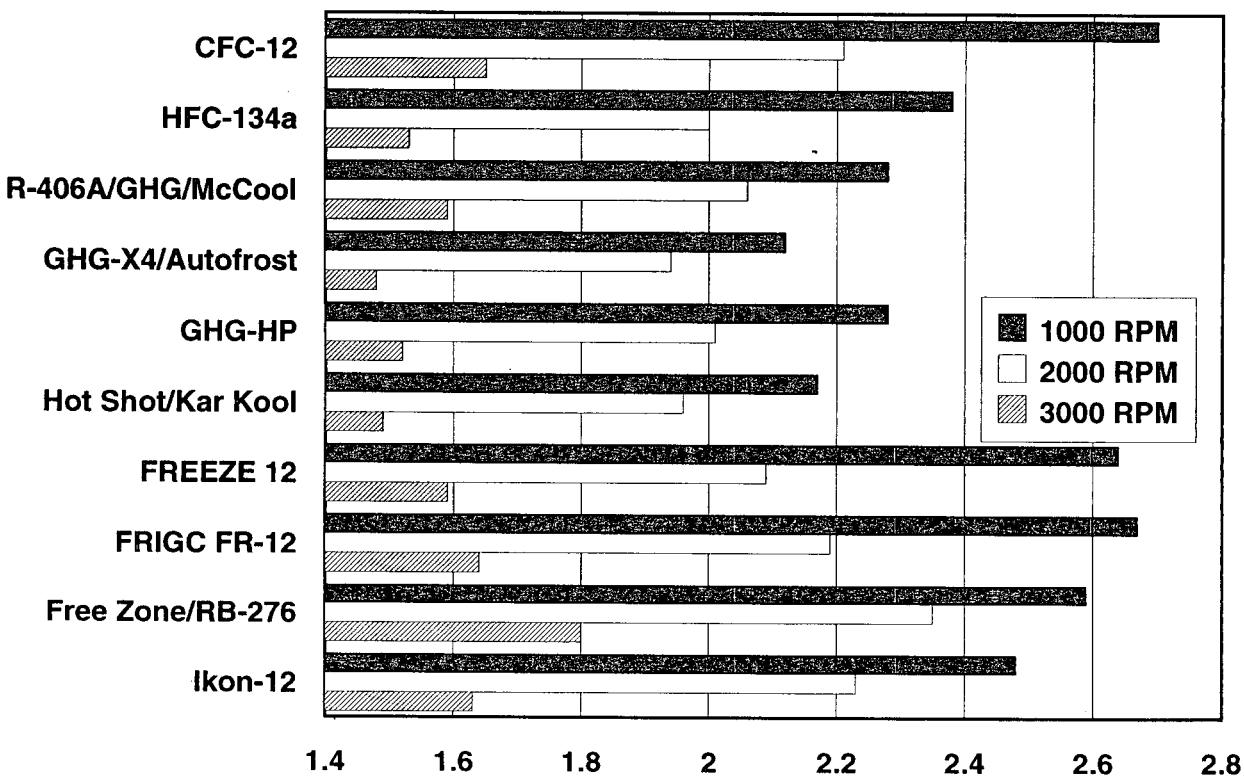

Figure 2. Coefficient of Performance

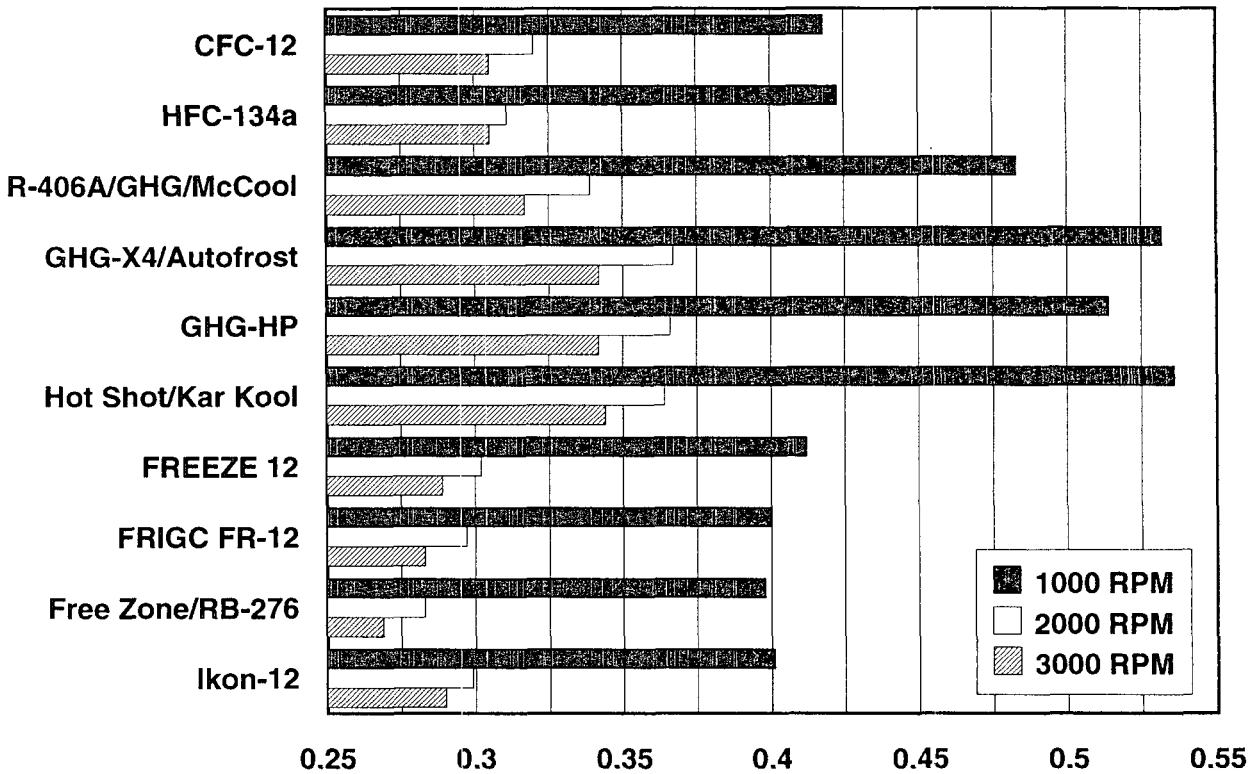

Figure 3. Evaporator Outlet Pressure (MPa)

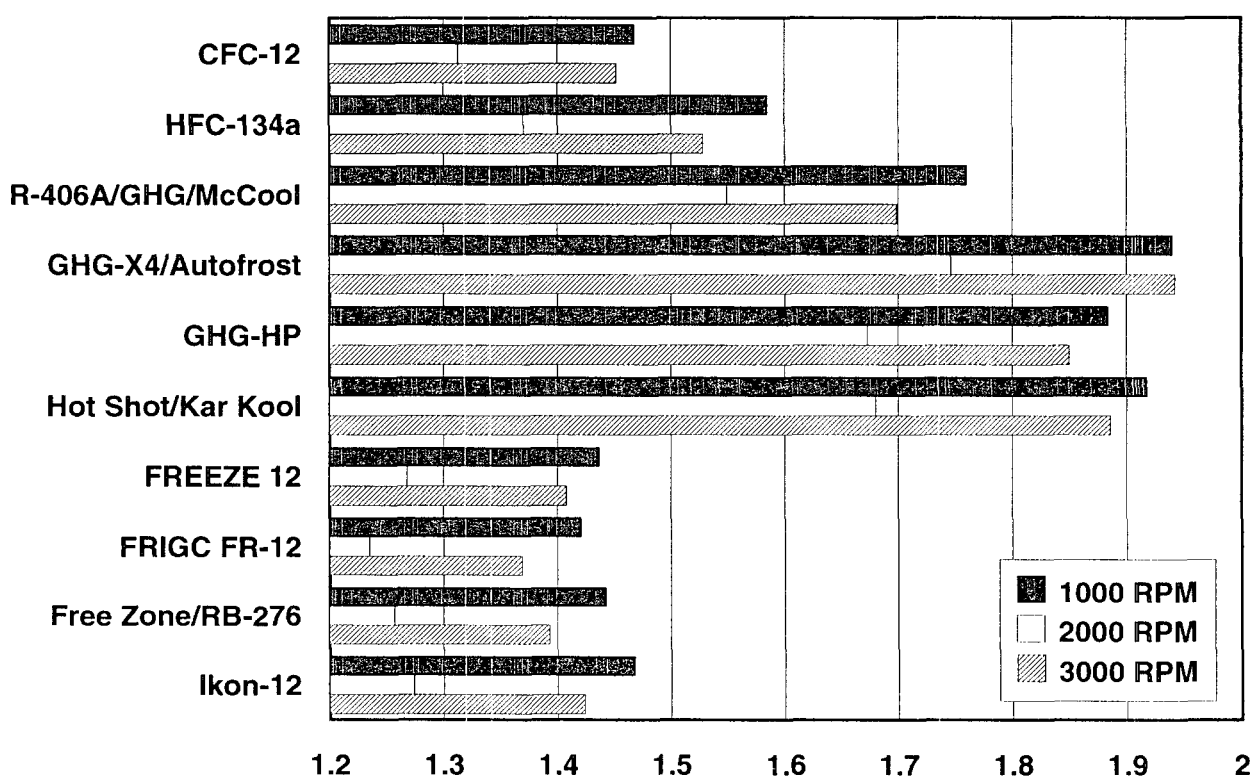

Figure 4. Compressor Discharge Pressure (MPa)

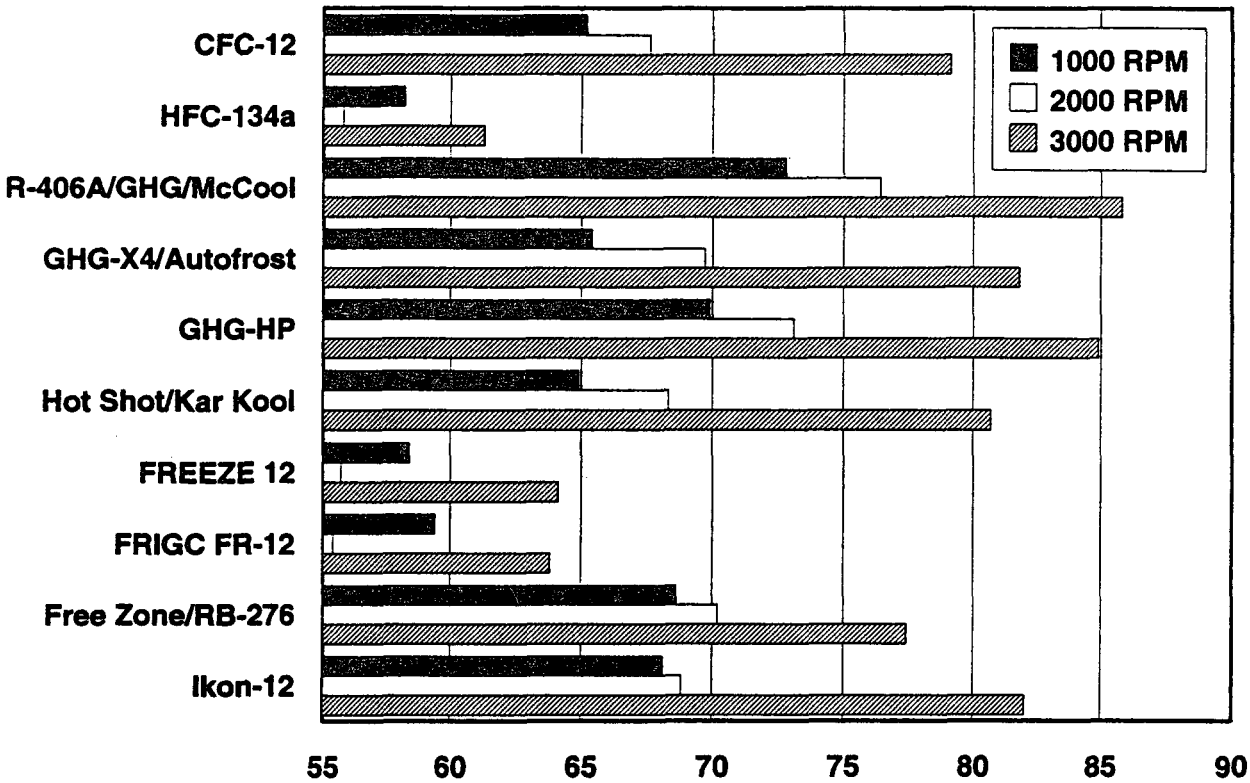

Figure 5. Compressor Discharge Temperature (Degrees Celsius)

Acknowledgment

The authors wish to acknowledge the assistance of Georgi S. Kazachki of Acurex Environmental Corporation, who provided technical consultation for performance testing.

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A HIGH-PRESSURE TRANSCRITICAL REFRIGERATION CYCLE WITH CARBON DIOXIDE FOR VEHICLE AIR CONDITIONING

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ABSTRACT

Carbon dioxide air conditioning units were installed in two city buses. The two buses were tested "on-the-road" during summer 1997 in Bad Hersfeld, Germany. By the end of August, the air condition systems of the two buses had been running together for more than 640 hours proving that CO_2-systems fulfill important on-the-road requirements. In the first part this paper presents and discusses typical on-the-road data. In the second part of the paper the compressor of the transcritical cycle is discussed in detail. Indicator diagrams were measured with the first and second generation of the compressor prototype. The comparison of the two compressor versions show significant differences in the measured indicator diagrams mainly due to the modified discharge valves.

INTRODUCTION

Unlike synthetically produced HFC-134a, carbon dioxide has a negligible global warming potential and it has no harmful breakdown products (see for instance McCulloch [1]). Carbon dioxide is a natural substance and does not have to be produced especially as refrigerant. It is available from natural wells or as a by-product from industrial processes. Hence, recycling of carbon dioxide is not necessary. That makes service and maintenance for CO_2 refrigeration and air condition systems very easy compared to systems which use synthetically produced refrigerants.

As a continuation of the papers presented at the 1995 and 1996 conferences (Köhler et al. [2] and Sonnekalb and Köhler [3]), this paper displays the most recent data collected from on-the-road tests with CO_2 bus air conditioning systems which operate with the so-called "transcritical cycle". In addition, indicator diagrams of the compressor are discussed.

ON-THE-ROAD TESTS WITH CARBON DIOXIDE AIR CONDITIONING SYSTEMS

In August 1996 the first carbon dioxide air conditioning system was installed in a bus (Bus A). This bus, a five year old city bus (Mercedes-Benz O 405) owned by the public transportation company in Bad Hersfeld, Germany, was displayed in September 1996 at the IAA (International Automobile Exhibition) in Hannover, Germany. A detailed description of the carbon dioxide air conditioning system was given by Sonnekalb and Köhler [3]. The authors presented experimental data of carbon dioxide prototypes measured in the laboratory and (installed in the bus) in the preheated environmental chamber.

In May 1997 two new buses (Mercedes-Benz O 405 N) were bought by the same public transportation company in Bad Hersfeld. These two buses are totally similar, except that one bus (Bus C) is equipped with a standard HFC-134a air conditioning system, whereas the second bus (Bus B) is air-conditioned by a CO_2 air conditioning system. The carbon dioxide system is identical with the HFC-134a-system regarding weight, overall size, blowers and fans, and (air-side) dimensions of the heat exchangers. The CO_2-compressor is smaller than the HFC-134a-compressor. With the help of these twin buses the "on-the-road"-behavior of the CO_2-system and the standard HFC-134a-system can be ideally compared. The bus with the carbon dioxide air conditioning system (Bus B) was displayed in May 1997 at the UITP congress and exhibition (International Union (Association) of Public Transport) in Stuttgart, Germany.

All three buses (Buses A, B, and C) are used for public transportation in Bad Hersfeld, Germany, all year round. By the end of August 1997 the air conditioning system of Bus A had been running for more than 440 hours. At the same time the air conditioning system of Bus B had been operating for more than 200 hours. In the following paragraphs typical measurement data are presented which were collected with the two CO_2-air-conditioned buses and the HFC-134a-air-conditioned bus in Bad Hersfeld during summer 1997.

Figure 1 shows the variation of the interior air temperatures of the two identical buses (Bus B and Bus C) for a typical hot summer day (August 11, 1997) in Bad Hersfeld, Germany. In addition, the variation of the ambient air temperature is also depicted in *Figure 1*. At that day the maximum ambient air temperature reached about 32 °C (90 F). The particular design aim in Germany for the (comparatively low) cooling capacity of city bus air conditioning units is to maintain an interior air temperature that is only 2 to 3 K below the ambient air temperature. Hence, on hot summer days the control system does not influence the comparison of the two buses, because for high ambient air temperatures the air condition units run with 100 % cooling capacity all the time. It can be clearly seen in *Figure 1* that most of the time the interior air temperatures of the two buses differ by less than 1 K. This shows that the on-the-road behavior of the carbon dioxide air conditioning system is comparable to that of a standard HFC-134a-system. As a matter of fact, the bus driver, who drove both buses and who did not know which bus was equipped with the carbon dioxide system, could not tell a difference between the two buses regarding their cooling performances.

Typical data of the variation of the compressor speed, the discharge and the suction pressure, and the gas cooler exit CO_2 temperature, and the ambient air temperature measured in Bus A are displayed in *Figure 2*. This data were collected in Bad Hersfeld on June 11, 1997 between 2:35 p.m. and 3:00 p.m. The compressor speed varied between idling speed (about 700 rpm) and the maximum speed of almost 3000 rpm. At 2:46 p.m. the air conditioning system was switched off for a short moment. The discharge and the suction pressure as well as the gas cooler exit CO_2 temperature were affected by the varying compressor speed. The gas cooler exit CO_2 temperature varied most of the time between 34 and 35 °C and followed the ambient air temperature. The temperature difference between the gas cooler exit CO_2 temperature and the ambient air temperature was about 2-3 K, resulting in an efficiency of the gas cooler heat exchanger of 90 to 95 %.

The suction pressure varied around 45 bar corresponding to an evaporating temperature of 10 °C (50 F). The discharge pressure varied around 85 bar. The critical pressure of carbon dioxide is about

74 bar. This means that the system operated in the transcritical mode. Unlike Evans-Perkins refrigeration cycles using HFC-134a, the COP of a transcritical refrigeration cycle has a maximum at an optimal high-side pressure. This optimal high-side pressure can be estimated with the help of a graphical method given by Inokuty [4-5] (the method is also described by Bhatti [6]). According to this method, a tangent is drawn to the isotherm of the gas cooler exit CO_2 temperature starting from the point of intersection of the 90 % quality line and the suction pressure line on the pressure-enthalpy diagram of carbon dioxide. The contact point of the tangent with the isotherm of the gas cooler exit CO_2 temperature gives the optimal compressor discharge pressure that will yield the maximum coefficient of performance for an ideal transcritical process (with a given gas cooler exit CO_2 temperature and a given evaporating pressure). With a gas cooler exit CO_2 temperature of 35 °C and an evaporating pressure of 45 bar Inokuty's method yields an optimum pressure of about 86 bar, which is very close to the actual measured high-side pressure. This is remarkable, because this CO_2-system was not equipped with a high-side pressure control. The high-side pressure was determined only by the refrigerant charge, which was optimized for this system.

The carbon dioxide air conditioning systems of the buses A and B were equipped with commercially available EGELHOF electronic expansion valves. These expansion valves were modified for the special carbon dioxide bus air conditioning application. It can be seen in *Figure 3* that this type of expansion valve is able to maintain the evaporator superheat between 6 and 11 K in spite of the significant variation of the compressor speed, and of the suction and discharge pressure. The expansion valve is well suited for highly transient operating conditions. The data shown in *Figure 3* (collected in Bus A in Bad Hersfeld on June 11 between 4:05 and 4:15 p.m.) are typical for the general behavior of the carbon dioxide air conditioning systems. The discharge pressure goes up and the suction pressure drops with increasing compressor speed.

COMPRESSOR INDICATOR DIAGRAMS

The compressor BOCK FKX3*CO2 was tested together with the whole air conditioning system in a calorimeter test cell and on-the-road. In addition to that, indicator diagrams were measured with the compressor, in order to evaluate the compressor in detail. The compressor was designed by the compressor manufacturer BOCK. They derived the CO_2-compressor from a standard two cylinder reciprocating compressor for HFC-134a. Virtually all major parts were reinforced (except of the crank shaft) and the displacement was reduced from originally 233 cc to 60 cc. Version 1 of this compressor was tested thoroughly in the laboratory and on-the-road. Based on this test, an improved version 2 was designed, with a reinforced lubrication system and modified valves. Version 1 had reed valves and version 2 had annular valves. A more detailed discussion of version 1 of this compressor was given by Süß and Kruse [7] and by Kaiser [8]. Version 2 of this compressor was discussed by Köhler et al. [9]. Version 2 was tested also comprehensively in the laboratory and on-the-road. By the end of August 1997, the total running hours of both compressor versions in the laboratory and on-the-road exceeded far more than 1000 hours. Version 2 of the compressor was also used with good results in a prototype transcritical refrigeration cycle designed for transport refrigeration. First experimental data of these laboratory tests in a calorimeter test cell were published by Sonnekalb and Köhler [10].

Figure 4 displays indicator diagrams for an ideal and a real compressor as plots of pressure inside the cylinder against the volume of vapor enclosed (see Gosney [11]). The ideal compressor is defined as one having no clearance remaining unswept at the end of delivery. Hence, the expansion process starting at the top dead center position is a vertical line. The induction takes place adiabatically at the constant pressure, p_1, measured in the suction pipe. The compression is an isentropic process. The delivery takes place adiabatically at the constant pressure, p_2, measured in the discharge pipe. The volume of vapor induced by the ideal compressor is denoted V'_A and is equal to the swept volume of the ideal compressor. The net ideal work which the piston has to do for the whole process is the shaded area on the indicator diagram for the ideal compressor:

$$W_{ideal} = -\int_{V'_A}^{V'_B} pdV\Big|_{s=const} + p_2V'_B - p_1V'_A = \int_{p_1}^{p_2} Vdp\Big|_{s=const} \tag{1}$$

In real compressors at the top dead center position there always remains a small volume of vapor (in the valve ports and in the space between the top of the piston and the cylinder head necessary to accommodate production tolerances), the clearance volume, which is inaccessible to the piston. The effect of clearance is shown in *Figure 4* on the diagram for the real compressor. The volume of vapor at the top dead center position expands as the piston moves outwards and the pressure of the vapor inside the cylinder does not fall immediately to p_1 but follows a polytropic expansion line. Also the compression is a polytropic process due to heat transfer between the vapor and the cylinder walls, and leakage. In addition to that, the suction and delivery do not take place at the constant pressures p_1 and p_2 respectively. A pressure difference between the vapor inside the cylinder and that outside is necessary to open the valves and to drive the vapor flow through the ports. Another difference between ideal and real compressors which appears on the indicator diagram is that the pressure at the bottom dead center position is not equal to the suction pressure p_1; i.e., the pressure inside the cylinder at the bottom dead center has not jet reached the pressure in the suction pipe. The net work which the piston has to do for the whole process in a real compressor is the shaded area on the indicator diagram for the real compressor:

$$W_{real} = \oint pdV\Big|_{measurement} \tag{2}$$

The ratio of the work of the ideal compressor to that of the real compressor is defined as the *indicated inner efficiency*:

$$\eta_{I,ind} = \frac{W_{ideal}}{W_{real}} \tag{3}$$

The suction valve opens at V_D and closes at V_A, so apparently the volume of vapor taken into the cylinder is $(V_A - V_D)$, which is equal to V'_A of the corresponding ideal compressor. The *indicated volumetric efficiency* is defined as the ratio of $(V_A - V_D)$ to the swept volume of the real compressor V_{swept}:

$$\eta_{V,ind} = \frac{V_A - V_D}{V_{swept}} \quad (4)$$

In *Figure 5* a typical comparison between the indicator diagram of version 1 and that of version 2 of the compressor BOCK FKX3*CO2 can be seen. The measured pressure inside the cylinder is plotted versus the dimensionless volume of vapor enclosed. In addition to that, the corresponding ideal process is also depicted on the diagram. Due to the modified valves the pressure drop across the discharge valves was significantly reduced in version 2 of the compressor. This results in an increase of the indicated inner efficiency. Version 1: $\eta_{I,ind} = 0.878$; Version 2: $\eta_{I,ind} = 0.934$. On the other hand, the valve modification increased the clearance which reduced the indicated volumetric efficiency. Version 1: $\eta_{V,ind} = 0.941$; Version 2: $\eta_{V,ind} = 0.815$. Due to measurement uncertainties, the overall error of these efficiencies was estimated to about 7 %.

CONCLUSIONS

On-the-road tests of two city buses equipped with transcritical refrigerating cycles using carbon dioxide as refrigerant showed no significant differences to buses equipped with standard HFC-134a air conditioning systems. The total on-the-road running time of the two air conditioning systems exceeded 640 hours. The expansion valve is well suited for highly transient operating conditions. Indicator diagram measurements of the compressor show high values for the indicated inner efficiency and the indicated volumetric efficiency.

ACKNOWLEDGMENT

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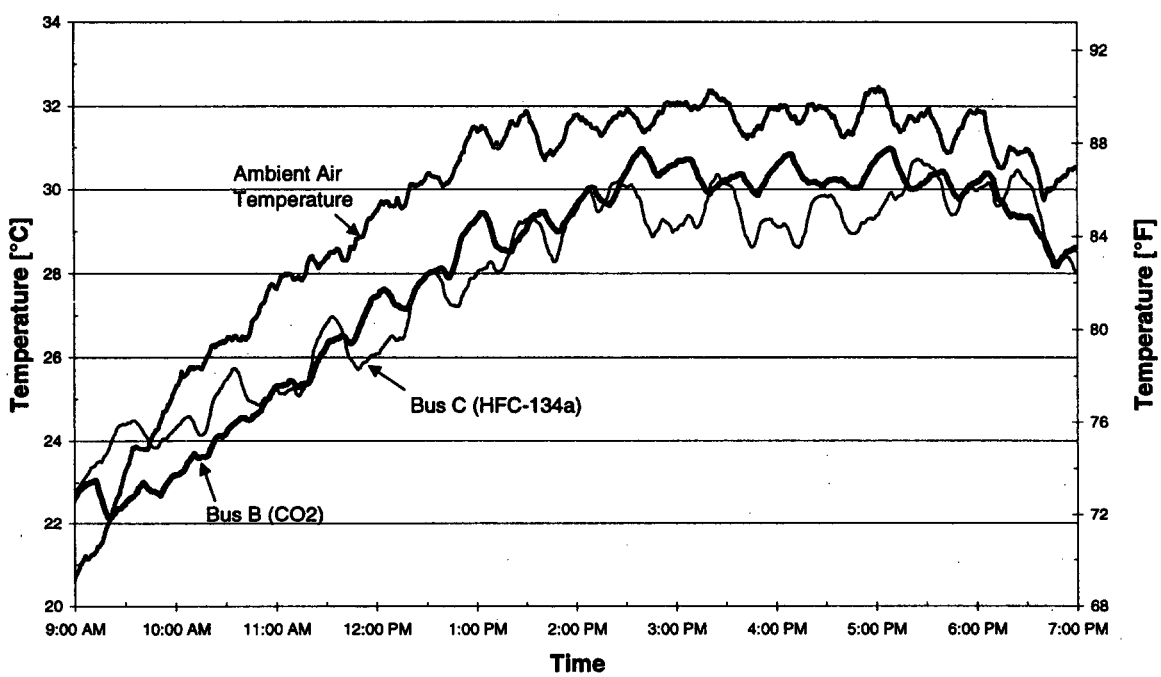


Figure 1: Variation of the Interior Air Temperatur of Bus B (Carbon Dioxide A/C System) and Bus C (Standard HFC-134a A/C System). Bad Hersfeld, August 11, 1997.

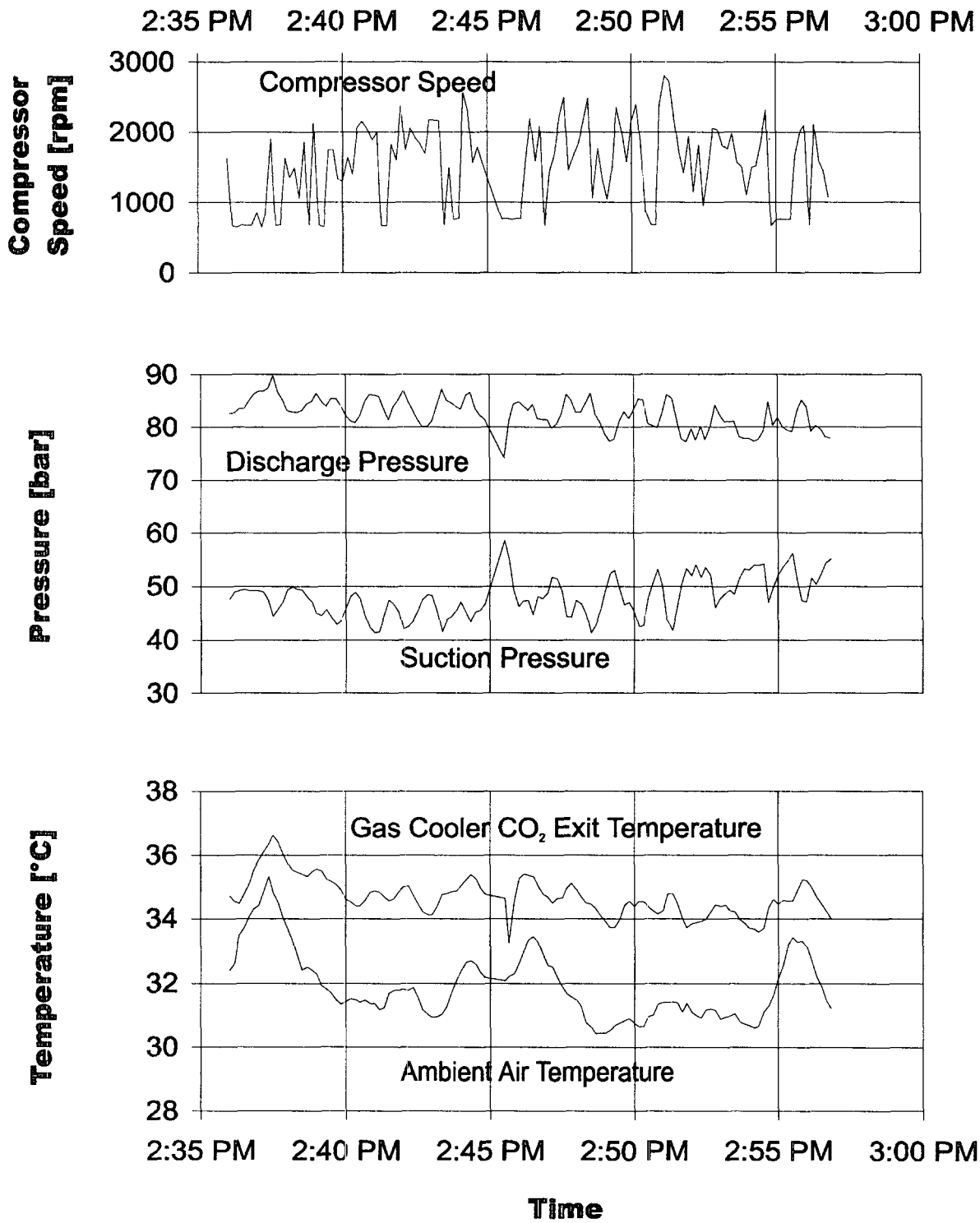


Figure 2: Time Dependent Variation of Compressor Speed, Pressures, Gas Cooler Exit CO_2 Temperature, and Ambient Air Temperature.
Bad Hersfeld, June 11, 1997.

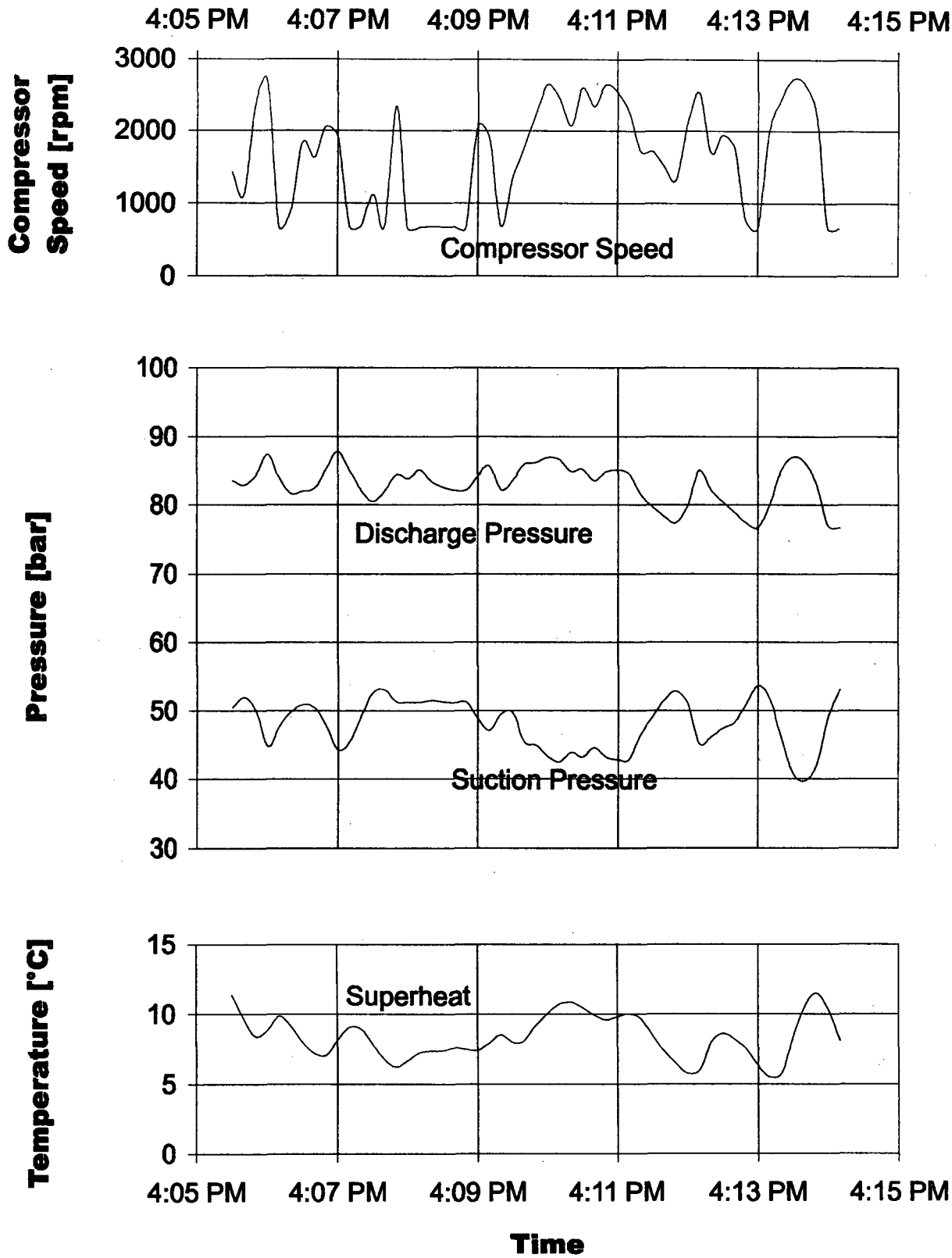


Figure 3: Time Dependent Variation of Compressor Speed, Pressures, and Superheat. Bad Hersfeld, June 11, 1997.

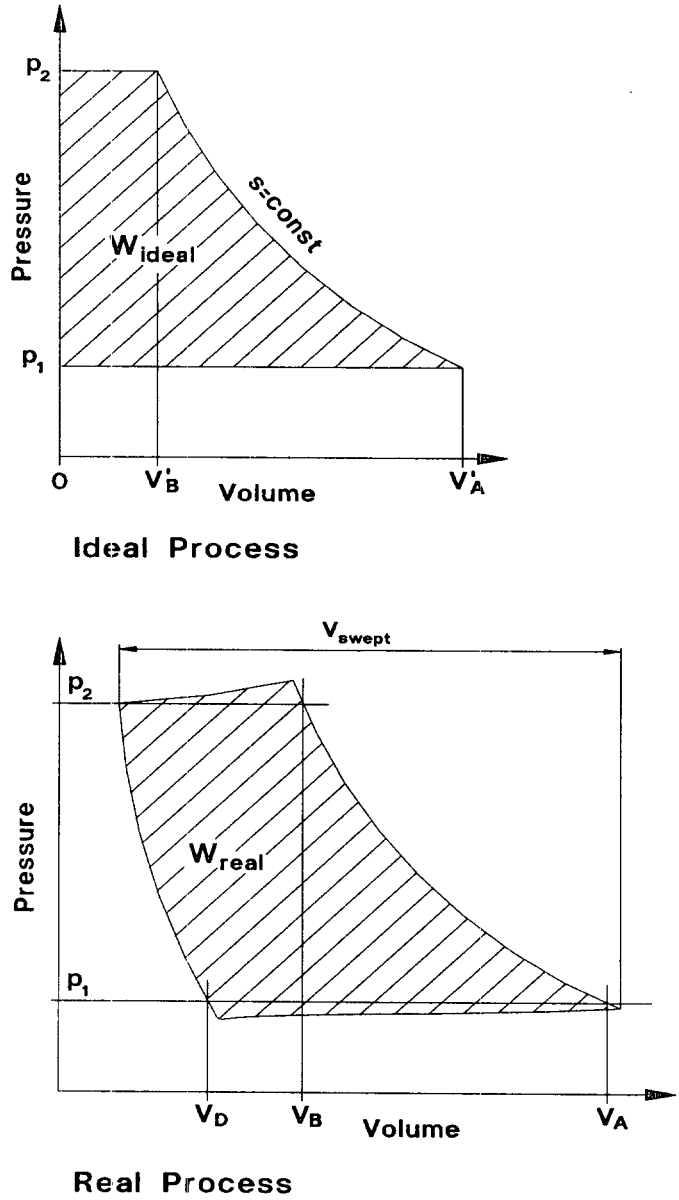
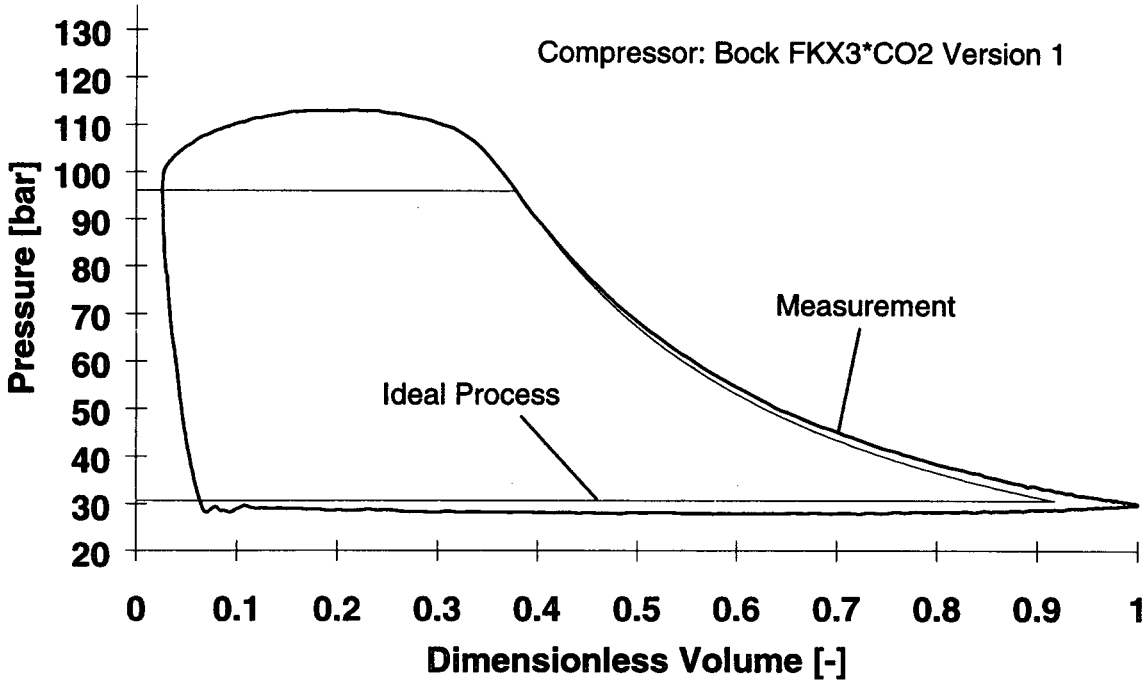


Figure 4: Indicator Diagram for an Ideal and a Real Compressor



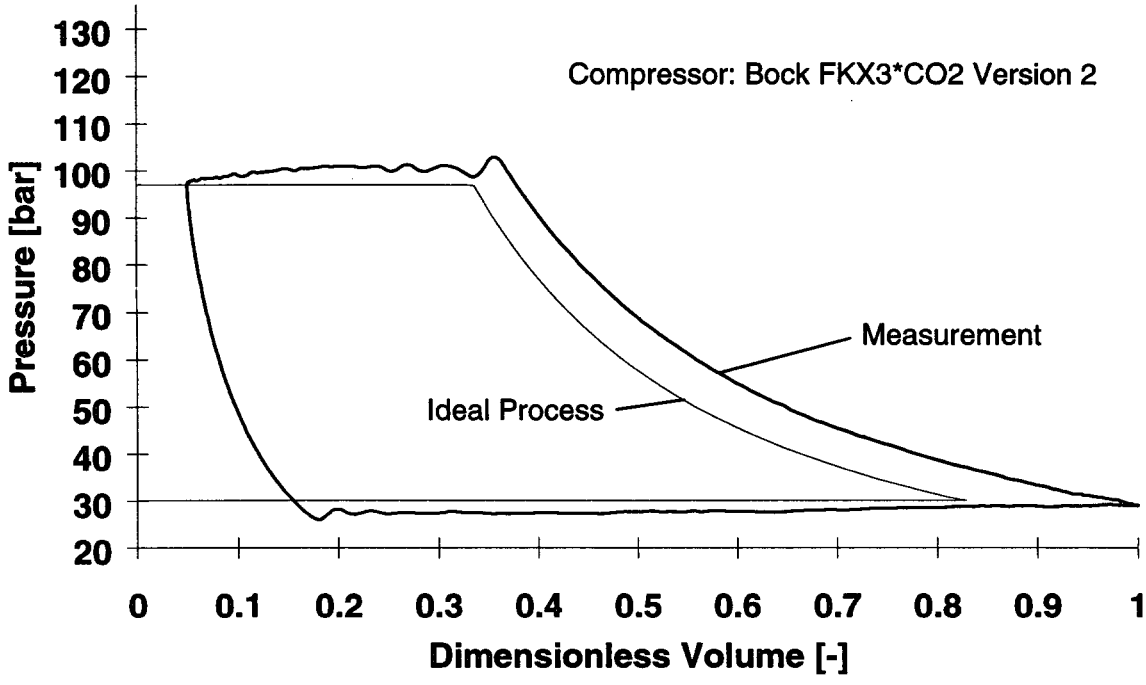


Figure 5: Measured Indicator Diagrams.
Comparison between Version 1 and Version 2 of the Compressor BOCK FKX3*CO2

New Test Bench for Measuring Leak Flow Rate of Mobile Air Conditioning Hoses and Fittings

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Introduction

Worldwide, the number of vehicles equipped with air conditioning systems is estimated at 300 millions, 50 % of them being in the United States. Refrigerant emissions are known to be very high but the average emissions per year are difficult to estimate. Evaluations vary between 150 g/yr and 400 g/yr.

Refrigerant emissions are due to several factors. Maintenance of systems is a key factor, and systematic policy of refrigerant recovery permits reduction of emissions of more than 50 % /1/. Netherveless automotive air conditioning systems exhibit characteristics that explain why these systems are more leak-prone than others. Three factors explain much of the emission of refrigerant : flexible hoses, rotating seal of the compressor and the very specific mounting of the engine and circuit components under the hood of the vehicle.

Leak-tightness of hoses is known to be poor. The test bench presented in this paper has been designed to measure leak flow rates of hoses. Its characteristic permits measuring independently the leak rate of the three major components of a hose which are :
- the hose itself, made of rubber or plastic;
- the crimp which connects the fitting and the hose, and
- the fitting.

1. USUAL MEASUREMENTS

Standard SAE J51 /4/ defines a method of measurement of hoses refrigerant emissions. The permeation test procedure can be summarized as follows : 4 parts of a hose are connected to create a volume filled with liquid refrigerant (in this case R134a) so that about 50% of the internal volume is occupied with liquid at room temperature. The test includes a 24-hour preconditioning period and a 72-hour mass loss period. Low pressure hoses are tested at a pressure corresponding to a saturation temperature of 80°C, that is 2,632 kPa for R134a. The permeation rate is measured by loss of mass. Maximum level of emissions are defined based on the hose materials and these levels are rather high.

The method is simple and can be used to distinguish between different materials of hoses but does not permit to measure the annual permeation rate of hose, crimp and fitting independently. To establish an accurate model of the permeation law for a given flexible material as a function of the pressure and the gas temperature it is necessary to gather more data.

2. PROPOSITION OF A NEW METHOD AND DESIGN OF A DEDICATED TEST BENCH

Since regulatory requirements are to be implemented to limit emissions of greenhouse gases, car manufacturers are willing to develop air conditioning systems with improved and guaranteed tightness. The Center of Energy Studies jointly with a manufacturer (Manuli) and state agencies, have initiated an approach to develop a leak rate measurement bench for components. The bench is designed for measuring leak rates of usual refrigerants between 1 and 100 g/yr. Characteristics of the bench include:
1. quantification of leak flow rates of a refrigerant,
2. variation of the internal pressure of the component to establish models of permeation laws as a function of the internal pressure,

3. tightness analysis of each component of the hose,
4. qualification of the circuit components for periods of time similar to the SAE J51 et J 2064.

2.1 Design of the test bench

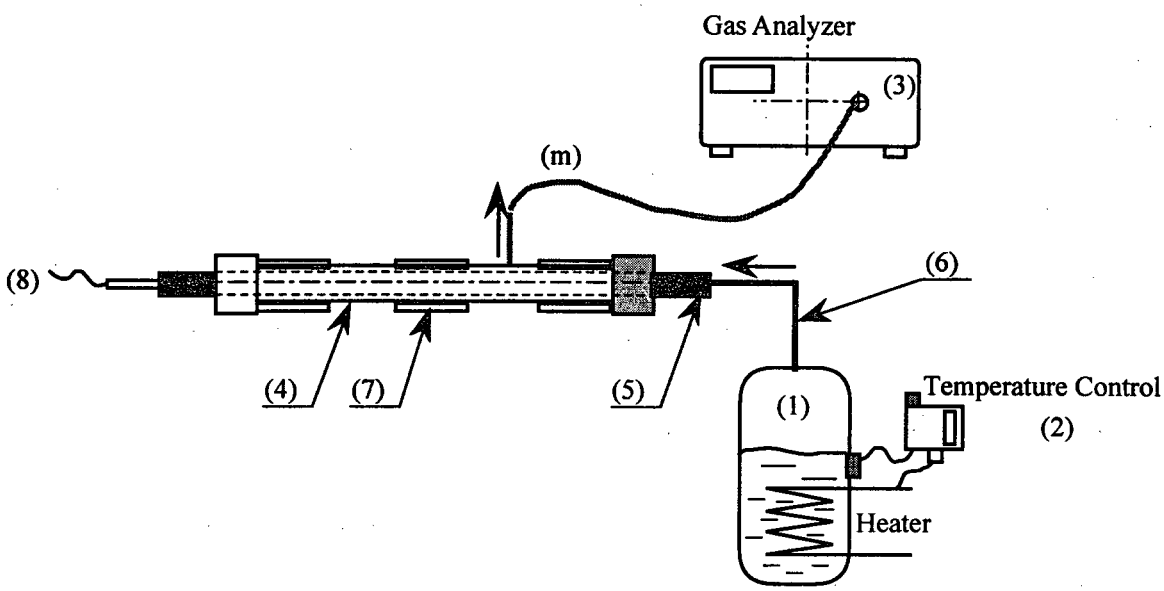

Figure 1 - The Test Bench.

As shown on Figure 1, major components of the test bench are detailed below.

- The vapor generator (1) is filled in with liquid refrigerant. This vapor generator is heated and the temperature is controlled.
- The component (5) is
  - connected to the vapor generator by a tube (6),
  - located in the control volume (4);
- the control volume is heated by electrical resistance with controlled temperature (7). A sensor (8) measures the temperature inside the component. This temperature has to be higher than the saturating temperature of the refrigerant so that there is no condensation. Gas leak is the worst case of tightness default. Internal pressure of the control volume is atmospheric pressure. The control volume is filled in with the "reference gas".
- A gas analyzer (3) - containing a thermal conductivity cell - is connected to the control volume and permits to measure the concentration of refrigerant sample taken from the control volume, at regular intervals.

Since volume, accumulation time and concentration are recorded, the leak rate of the component can be defined. The test bench can be calibrated at any time with calibrated concentration samples.

3. PRELIMINARY RESULTS

In order to have an acceptable accumulation time, the control volume surrounding the component has to be as small as possible. So a control volume is created for each of type of component. The control volume is kept at atmospheric pressure but the leak flow creates a small increase of pressure. When the accuracy range of pressure gauges permits measurement of small variations, concentrations can be correlated with pressure variations of the control volume.

The pressure in the control volume is close to atmospheric pressure. The leak tightness between the control volume, the component and the surrounding atmosphere is not too difficult to realize because the pressure variation is close to zero. But diffusion shall be taken into account and labyrinth-type fittings are necessary to monitor leak tightness of the control volume.

3.1 Hose

Figure 2 shows permeation rates of two different technologies of hoses. Variations of the leak rate in g/yr are expressed as a function of the internal pressure. Curves have been obtained after performing 5 series of measurements on the two types of hoses. Pressure inside the hoses were selected between 10 and 26 bar. (kPa)

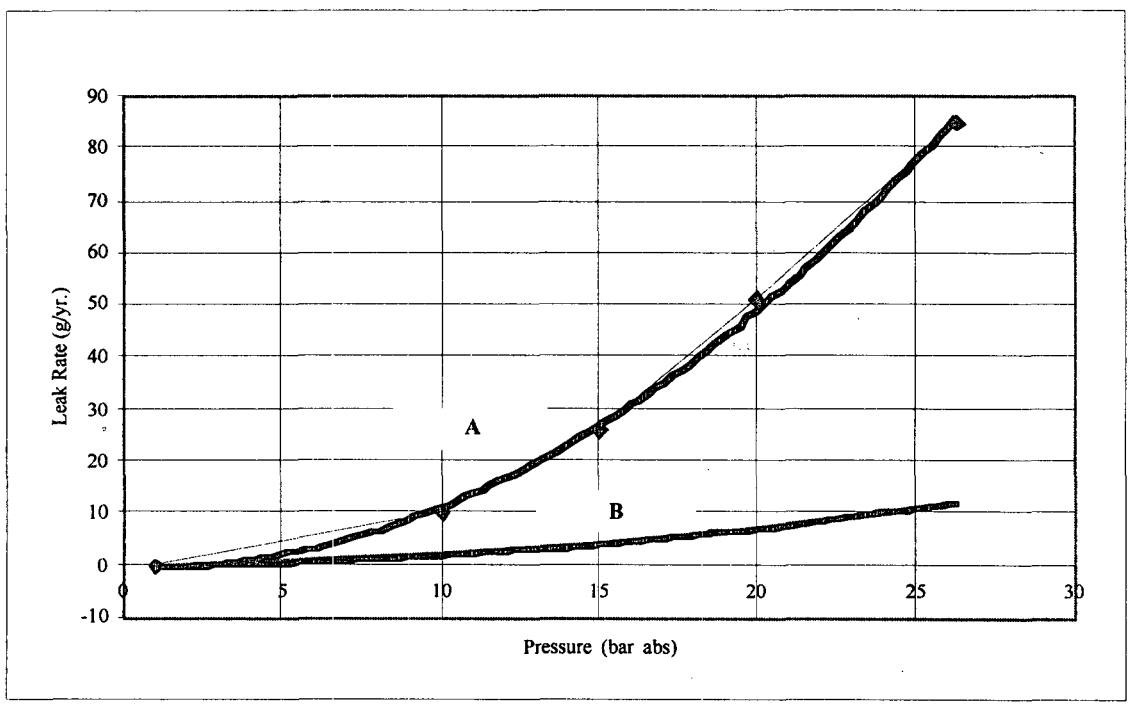

Figure 2 - Variations of the Leak Rate as a Function of the Pressure for two Types of Hoses.

The analysis of the results shows that:

1. Curve of hose "A" is a quadratic law in agreement with the general equation herebelow :

$$\dot{G} = \frac{\dot{m}}{\rho_u} = \frac{\pi\ d^4}{128\ e\ \mu}\ \frac{(p_{int}^2 - p_{atm}^2)}{2} \qquad (1)$$

where:

d	diameter of the leak channel (m)
e	material thickness (m)
$\dot{m}$	is the mass flow rate (g/yr);
p_{int}	internal pressure of the hose
p_{atm}	atmospheric pressure of the control volume
μ	is the refrigerant viscosity (Pa•s)
ρ_u	unitary density (kg/m3•Pa)

The flow rate of the refrigerant is proportional to the difference of the squares of the internal pressure of the hose and the atmospheric pressure in the control volume.

2. Permeation rate depends on the hose technology : between hose "A" and hose "B" the permation ratio is 9. This ratio does not apply respectively to the costs of the hoses.

3. The leak flow rate is very dependent on pressure. This implies that technological effort should be emphasized on tightness of the discharge hose of the compressor.

This data permits more realistic simulations on annual permeation rate of hose.

3.2 Hose Fittings

Three types of hose fittings were tested, each of them being tightened using a torque wrench and with two different torques. Results of the tests are presented in Figure 3.

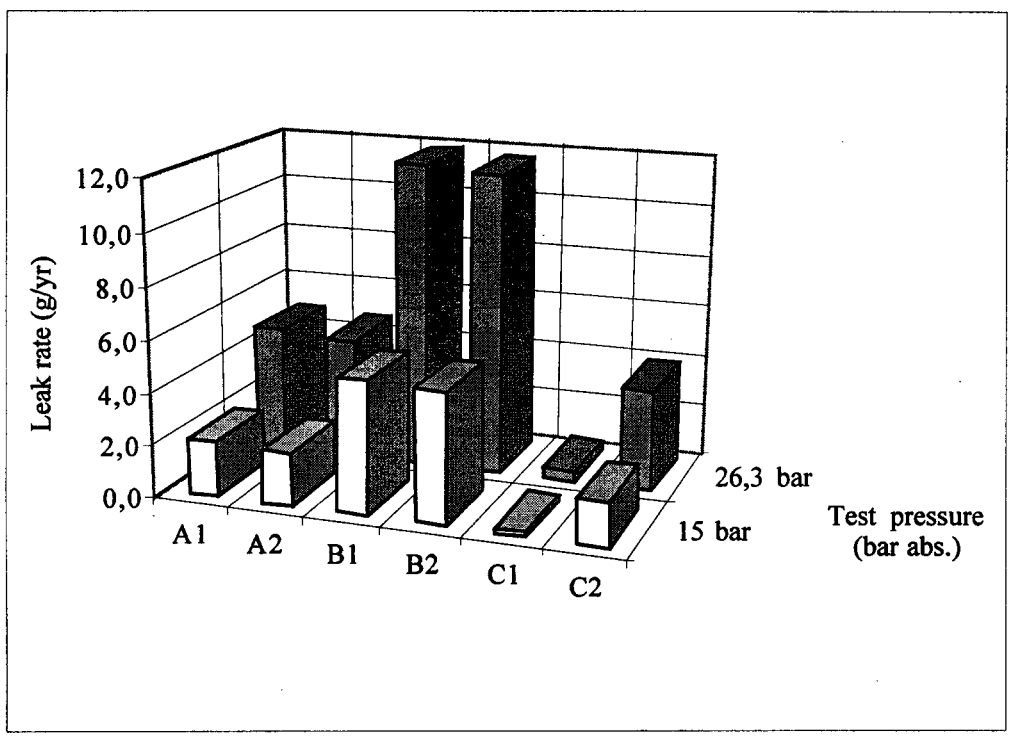

Figure 3 - Variations of Leak Rates of Three Fittings at Two Different Pressures.

Figure 3 gives three major information.
1. Leak rates are far lower than permeation rate of hoses.
2. Hose fittings "A" and "B" have identical behaviour whatever the torque, while C is sensitive to the torque
3. The leak rate of these componants is low if they are correctly set and tightened with the appropriate torque.

3.3 Crimp

Three types of crimps were tested. As per hose fittings leak rates are low compared to permeation rates of hoses. Only tests performed at 26 bar were significant.

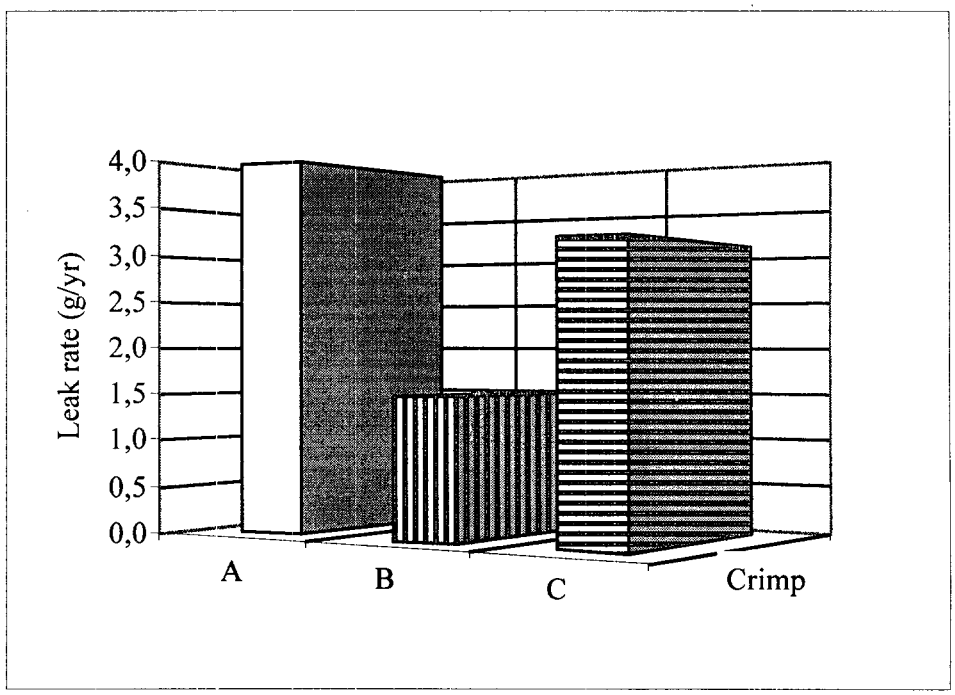

Figure 4 - Variation of Leak Rates on Double Crimps.

4. Annual simulation of emissions

As in reference /2/, assume the following hypotheses :
- Operation time of the air conditioning system : 200 hours/year
- Operation time of the vehicle without air conditioning : 400 hours/year
- Idle time : 8 160 hours/year

The refrigerant is R134a.

Average temperatures
- 15 °C when the vehicle is not operating;
- 38 °C when the vehicle is operating but the air conditioning system is turned off;
- 105 °C and pressure 26.3 bar for the discharge hose,
  45 °C et 11.6 bar for the liquid hose and
  35 °C et 3.5 bar for the suction hose when the air conditioning system is on.

Simulations take into account the variation of pressure due to the three main test conditions:
- mobile air conditioning in operation;
- mobile air conditioning off and vehicule running;
- vehicle at standstill.

Also simulations are performed for three different conditions of pressure (discharge and suction lines for gas, and the high pressure liquid line). The air conditioning system tested is composed of 8 fittings, 8 crimps and three hoses.

Results of simulations

Line	T °C	P bar	$\dot{m}$ hose (g/yr)		$\dot{m}$ fittings (g/yr)		$\dot{m}$ crimps (g/yr)	
			A	B	B	C	A	B
Discharge	105	26,3	2	0.2	0.8	0.05	0.3	0.1
Suction	35	3,5	-	-	-	-	-	-
Liquid	45	11,6	0.3	0.05	0.2	-	-	-
Total			2.3	0.25	1	0.05	0.3	0.1

Table 1 - Tests Performed with Air Conditioning System On.

Line	T (°C)	Pint (bar)	$\dot{m}$ hose (g/yr)	$\dot{m}$ fittings (g/yr)	$\dot{m}$ crimp (g/yr)	Total (g/yr)
ABA	40	10.2	1.6	0.6	0.2	2.4
BCB	40	10.2	2	0.05	0.1	0.35

Table 2 - Tests Performed with Air Conditioning System Off and Vehicle Operation Time of 400 hrs.

Line	T (°C)	Pint (bar)	$\dot{m}$ hose (g/yr)	$\dot{m}$ fittings (g/yr)	$\dot{m}$ crimp (g/yr)	Total (g/yr)
ABA	15	4.9	8.2	3.1	1	12.3
BCB	15	4.9	1	0.2	0.4	1.6

Table 3 - Tests Performed with Air Conditioning System Off and Vehicle Operation Time 8,160 hrs.

Results presented on Figures 2, 3 and 4 permit classifying the three components from the most leak tight to the less leak tight.

The two following extreme assemblings were simulated :

- the worst case (noted ABA) is composed of the less leak tight components: hose A, fitting B and crimp A. This combination gives a leak rate of 18.3 g/yr (3,6 + 2,4 + 12,3);
- the best case (noted BCB) is composed of the best leak tight components: hose B, fitting C and crimp B. The leak rate of this combination is 2.35 g/yr (0,4 + 0,35 + 1,6).

The tests indicate that

- even in the worst assembling the emission rate of hose, fitting and crimp is well below the emission rate usually known and labelled;
- a ratio of 8 exists between the best and the worst components assemblings.

It appears necessary to develop additional studies to permit predicting tightness degradations of components induced by mechanical stress (expansion, contraction) due to on/off cycles of the air conditioning system but also to the system vibrations. One can suspect that a lot of leak tightness degradations are induced by a poor tightening of components.

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PROFILE OF AUTOFROST® REFRIGERANTS

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ABSTRACT

Autofrost refers to a family of zeotropic refrigerants marketed by Monroe Airtech, Bloomington, IN, and their subdistributors. Autofrost-X3 (R-406A), Autofrost-X4 (pending ASHRAE Standards 34 committee as R-414A), GHG-X5, and GHG-HP refrigerant will be discussed. Used refrigerant return/reclaim policies along with warranties and availability of product will be discussed along with performance.

INTRODUCTION

Autofrost refrigerants are designed as high performance direct replacements for CFC-12 and R-500, and with some retrofit effort (removing PAG oil) for poorly performing R-134a systems. All Autofrost refrigerants require no oil changes as they operate well in mineral oil (or alkylbenzene oil) found in CFC-12 systems. These refrigerants are all EPA SNAP acceptable for stationary applications and acceptable with use restrictions for the MVAC sector. Performance is equal to or often better than that of the original CFC-12 system. Autofrost-X3 (R-406A) was developed in 1990 and was first known as "GHG Refrigerant-12 Substitute"[1].

Reclaiming Policy

Monroe Air Tech, Inc. (master distributor for Autofrost refrigerants) will accept all used refrigerants (even if not Autofrost) from their refrigerant customers regardless of purity or flammability. Customer pays freight to Monroe. However, Monroe may have a local distributor available. Call 800-424-3836 for shipping instructions, paperwork, boxes and material. Monroe will test each cylinder for composition. Credit will be issued immediately toward purchase of virgin Autofrost. Credit will range from $1.65 to $7.00 per pound depending on percentages of components (i.e. pure R-12 is $7.00 per pound). Cylinders will be purged with nitrogen and checked for certification. If needed, re-certification is available for $20. Cylinders are returned within 10 days, freight prepaid. Reclaimers can now separate out mixed refrigerants, even blends of R-12/R-22.

The Authors' Views on Fittings/Recycling/Recovery/Reclaiming MVAC Refrigerant.

Since the public can legally buy R-134a (with no certification) or most any other refrigerant after passing the easy EPA 609 MVAC Technician test (open book test for $10 - $20, even available on the Internet), the current regulations of fittings, labels, etc, to "prevent contamination", are being thwarted and are not serving the purpose for which they were intended..

Some cars, including Ford Tauruses, some 92-93 Honda Accords and some 90-92 Toyota Celicas, have R-12 access ports that run along the top of the radiator or other areas with very little hood clearance. Adding on any retrofit fitting for R-134a or other refrigerant, results in not being able to close the hood. In general, the public (do-it-yourselfers "DIYers"), after having obtained (legally or illegally) refrigerants by whatever means, usually totally disregard EPA regulations on venting, fittings, and labeling for MVACs. "Permanently attached" fittings are often easily removed with a wrench or a little heat, and labels will often fall off or be removed on purpose. When the service fittings are beat-up, the retrofit fittings may fail to work or cause leaks.

Another issue with the "Permanently Attached Fittings" part of the current EPA retrofit regulations is that a "restraint of trade" issue is involved. Assume, that John Citizen takes his car to Joe's Service Station for a gasoline fill-up, and unbeknownst to Mr. Citizen, Joe's Service Station "Permanently Attaches" a filler neck fitting to Mr. Citizen's car, such that it accepts only filler hoses from Joe's stations. Now Mr. Citizen MUST buy his gasoline at Joe's. This is restraint of trade. Mr. Citizen takes his car in for A/C work, and Joe's Garage does an EPA regulation retrofit to alternative refrigerant X (including permanently attached unique threaded fittings for refrigerant X). Mr. Citizen is not happy with the performance of refrigerant X or he needs service and has traveled to an area where refrigerant X is not available. Mr. Citizen becomes frustrated with refrigerant X's poor cooling, finds another shop and wants refrigerant Y installed for better performance. What is the second shop going to do with the permanently attached fittings for refrigerant X? What if he/she does not have adapters for them? "Leak of Convenience" (illegal venting)? In this predicament, changing to another refrigerant would incur major costs of subassembly, labor and possible condenser replacement; all because "permanently attached" fittings can not be removed. This raises the issue of "restraint of trade".

If the EPA had allowed the unique threaded fittings to be attached "non permanently", the restraint of trade issues and a large number of "Leaks of Convenience" would be eliminated. Unique fittings serve as a unique "label" to identify the alternative refrigerant. They will tend not to fall off as often as labels.

The air shop mechanic very often has to face the "unknown refrigerant" question in an incoming vehicle for A/C service. Given the nearly total disregard for EPA fittings and labeling regulations by DIYers, air shops still might want to purchase a basic refrigerant identifier. Current identifiers will not often accurately identify the current compositions of mixed refrigerants, and blends. Blend compositions in vapor space are different than in liquid space and the result is very temperature dependent. Leaking (fractionation) further complicates the issue. It is difficult to properly identify these compositions even with expensive equipment (Gas Chromatographs) and trained operators. All the identifier really needs to do is to tell you whether you have pure R-12, R-134a or something else. Easy enough, even for the basic identifiers.

Pure R-12 can then be recovered and be sent to a reclaimer or recycled on site. Anything else can be recovered into a "mixed refrigerants" cylinder and sent to a reclaimer. R-134a is so cheap now, that on site recycling makes little economic sense. The authors strongly feel that any refrigerant should not be recycled on site, but instead be recovered and sold to a reclaimer. When one gets an oil change, the shop does NOT NEED DIFFERENT recovery machines for each type of oil. It is not necessary to "recycle" it on site and reintroduce it into cars at oil change time. Instead, all the oil can be collected in one bucket and sent off for rerefining (reclaiming). In many cases, it doesn't even make economic sense to purchase a refrigerant identifier. Just recover ALL refrigerants into a single cylinder and return to a reclaimer for separation and cleaning. Considering that most cars come in "empty" or with at most ½ the charge; it takes a lot of recovered R-12 to pay for a refrigerant identifier.

Visits to twelve air shops in 1993/4 showed that all of them had "wet" dry eyes (moisture indicators) on their recycling equipment. When technicians were asked about the last time they changed their dryers; most of them, surprised, exclaimed: "WHAT DRYERS?". The authors feel that the current MVAC recycling program causes extensive damage and venting of CFC-12 due to moisture and acids being passed from customer to customer. Moisture laden refrigerant (except for 100% hydrocarbon blends) slowly hydrolyzes to form acids (hydrochloric and hydrofluoric) and "sludges" (aluminum chloride and fluoride). The acids corrode the insides of the system, often causing leaks, thus venting the charges and the sludges plug up expansion devices, compressors, or dryers/accumulators, and results in system failure. The damaging effects of "wet" refrigerant often take a few months to surface, so blame is often wrongly directed toward the car maker instead of the mechanic/air shop. POE (ester) and PAG oils are extremely hygroscopic and absorb large amounts of moisture when the system is "open" for service. Wet refrigerant generates lots of repeat business the following season. "Wet" PAG oils often turn bright orange. Unless a complete flush (including compressor) and dryer change is done, after PAG oil is wet (system open for days or weeks), the wet oil will begin the acid destruction problems again at the completion of service to be repeated ad infinitum. The extreme moisture sensitivity of PAG and POE oils compared to mineral oil make R-134a failures of this type occur more often. Mineral oil is fairly resistant to absorbing moisture when in open containers or systems. A dryer change followed by a good vacuum would result in a stable R-12 system for many years.

These problems are solved in a large part, by using the recover/reclaim route for *ALL REFRIGERANTS*. The equipment outlay for the air shop is minimal, with only a single "recover only" machine, at less than $1000, compared to many thousands of dollars for multiple recycling machines and the hassles of maintaining them. Reclaimers have the proper equipment to know when refrigerant purity has been achieved and they operate under ARI-700 [2] specifications for moisture, acids, and a number of other contaminates. Reclaimed refrigerant is often more pure than virgin refrigerant. Much reclaimed refrigerant just "disappears" into the feed streams of new (virgin) refrigerants (after first being cleaned and moisture removed) at below contaminate specifications (1/2%).

The problems of mixed refrigerants[3] and "contamination" have been blown way out of proportion by some segments of the industry. The main concern is keeping chlorinated refrigerants (CFCs, HCFCs) out of systems with PAG oil (R-134a new or some retrofits) as most PAG oils are broken down by these refrigerants. One PAG oil, DAPHNE, has literature stating resistance to chlorinated refrigerants, but one often does not know which brand of PAG oil a car contains before service. Running 100% R-134a in mineral oil in an R-12 system, as has been the case for DIYers, usually results in compressor failure after a few days since R-134a will not return the mineral oil to the compressor. Outside of these cases, mixing refrigerants (in R-12 mineral oil systems) often works acceptably. As long as 5% to 10% R-12 remains, R-12 mineral oil systems can be "topped off" with R-134a (illegally by DIYers) and they offer reasonable performance. The real enemy of system longevity is moisture.

Performance

All Autofrost refrigerants are zeotropic, and have "glides" in the order of 15° F. This increases the phase change area in the condenser compared to single component refrigerants. The increased phased change area enables the condenser to reject more heat and therefore better cooling capacities are provided. Duct temperatures 3° F to 8° F colder than R-12 are common. R-406A/Autofrost-X3 typically performs 8° F to 12° F colder duct temperatures than R-134a and 12° F to about 15° F colder than R-134a based blends.

R-134a and especially the R-134a based blends operate with evaporator pressures too low in R-12 systems. This necessitates changing the low pressure cutout switch from 24 PSIG to 14 PSIG (R-134a blends) and about 20 PSIG (R-134a). Even with the low pressure cutout changed, the R-134a based blends will still get "cold" given enough time, but capacity is reduced due to lower mass flows. If the low pressure cutoff switch is not changed, R-134a based blends will constantly cycle the clutch during normal operation, with greatly increased clutch failure rates. For variable displacement type compressors (GM V5), the suction pressure is set at 28 PSIG, and cannot be easily changed. These systems will have greatly reduced capacity with R-134a and even worse performance with R-134a based blends.

The authors have encountered numerous R-134a systems, both new and retrofitted that have performed poorly[4]. Others have performed well. Several technicians have "reverse-retrofitted" some of these systems to Autofrost refrigerants with excellent results. The hardest task is to remove ALL of the PAG oil if installed in the system. Autofrost contains HCFCs which destroy most PAG oils. The system must be disassembled and flushed, with the compressor put on the bench and turned over 40 or 50 times while dribbling mineral oil into the intake. Experience has shown that the standard 525 SUS mineral oil used in R-12 systems has sometimes been too thick for the tighter tolerances of new R-134a compressors, causing near immediate failure. However, a thinner mineral oil, such as Ford part #YN9, has been found to work well in all systems. R-134a systems with POE oil, should have some of the oil drained if easily accessible, with the drained oil replaced with mineral oil as above.

Autofrost refrigerants

Blend compositions in weight percentages								
Refrigerant	R22	R142b	R124	R227ea	R600a	GWP	ODP	Comments
GHG-X3 Autofrost-X3	55	41			04	1560	.055	R406A – best thermodynamics, least cost
GHG-X4 Autofrost-X4	51	16.5	28.5		04	1200	.045	(Pending as R414A) – UL "practically nonflammable"
GHG-HP	65	31			04	1530	.053	Extreme performance for hot,humid climates requires "defrost" timer to prevent evap freezeups. 25° F duct temps.
GHG-X5	41	15		40	04	2045	.0304	High molecular weight, useful for centrifugal chillers
R-12	-	-	-	-	-	8100	.9	CFC-12 for comparison
R-134a	-	-	-	-	-	1300	0.0	HFC-134a for comparison

GWPs are 100 year based on mass fractions of blend components calculated on data from [5]. ODPs are the "semi-empirical" method based on mass fractions of blend components calculated on data from [6].

Autofrost-X4 offers nearly the same performance as Autofrost-X3, and it carries an UnderWriters Labs (UL) classification of "Practically Nonflammable" (same as R-22). Autofrost-X4 is also marketed as "Chillit" by McMullen Oil products of Clearwater, FL. GHG-HP is basically R-406A with 10% more R-22. HP *requires* a working high pressure cutoff switch since it runs higher pressures. Some systems (especially variable displacement compressors, continuous run) may need a "defrost timer" to be installed. This simple device installs in series with the compressor clutch circuit, and turns off the compressor for 15 seconds every 4 or 5 minutes to allow ice to clear from the evaporator. GHG-HP has demonstrated 25° F duct temperatures (MAX RECIRCULATE) in 100°F humid ambients, such as south Florida and Texas. GHG-X5 offers similar performance to Autofrost-X4 in reciprocating compressors. Due to its high molecular weight, GHG-X5 offers better performance in Centrifugal Chillers.

R-406A is comprised only of "old" molecules, ones that have been in use for decades, with toxicity characteristics well established. Some "new" molecules may be more likely to turn up surprises in the toxicity area. A recent article in the British medical journal, *The Lancet,* has reported cases of liver damage (symptoms of acute hepatitis) in nine human workers after exposure to mixtures of R-123 and R-124 [7]. The authors of [7] raise concerns on the toxicity of R-123/R-124 in human beings and urge urgent development of safer alternatives. Many current R-12 substitute blends on the market contain large amounts of R-124 (R-401A/B/C, R-409A, FRIGC® FR-12, R-414A (Autofrost-X4), R-414B (Hotshot), etc). R-406A (Autofrost-X3) contains no R-124.

Availability, Warranties, and Compatibility

Autofrost (R-406A) is available nationwide through National Refrigerants (United Refrigeration) and through wholesalers such as United Suppliers of America and ATC Specialists. Call Monroe Air Tech at 800-424-3836 for availability information. Monroe Air Tech warrants Autofrost to offer better performance than R-12 and R-134a refrigerant as well as warranting compressors against failures caused by the refrigerant.

In general, almost all O-rings and compressor shaft seals work well with Autofrost refrigerants. Buna-N, and HNBR (light green) seals and O-rings should be avoided. Neoprene is the most preferred material (blue O-rings). HNBR has only appeared in recent times though.

Conclusion

The family of Autofrost refrigerants provides suitable direct replacements for CFC-12 (and R-500) over a wide variety of applications and conditions without having to add or change out lubricants.

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1997 INTERNATIONAL CONFERENCE ON OZONE PROTECTION TECHNOLOGIES

BALTIMORE, MARYLAND
NOVEMBER 12-13, 1997

FREEZE 12®

ANSWERING THE CALL FOR AN ALTERNATIVE REFRIGERANT

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INTRODUCTION

Freeze 12® is an EPA acceptable CFC alternative refrigerant blended and packaged by Technical Chemical Company (TCC). Based in Dallas, Texas, TCC is a privately owned company with branch locations in Los Angeles, California and Orlando, Florida. TCC is a world leader in refrigerant packaging with private label customers which have included Ford, Toyota, ICI and John Deere to name a few. TCC markets it's products under the Sercon and Johnsen's logos. TCC is the manufacturer of the Sercon line of Refrigerant Recovery/Recycle Equipment and also offers a full line of A/C service tools and accessories. In addition, we blend and package a variety of automotive service chemicals including PAG and Polyol ester A/C lubricants.

THE NEED FOR A CHOICE

Since 1995, all original equipment manufacturers (OEMs), both domestic and import are producing vehicles equipped with A/C systems designed specifically for HFC-134a. Currently, HFC-134a is the only refrigerant recommended by the vehicle manufacturers for retrofit applications. For some vehicle platforms, retrofitting to HFC-134a is not a recommended procedure by the OEMs. In these cases, the recommendation is to stay with CFC-12 for the remaining life of the vehicle. Retrofitting to HFC-134a is not recommended for many older vehicles (as well as some newer vehicles) where increased discharge pressures due to a lack of adequate condensing may place too heavy of a load on the existing hoses and/or compressor and cause premature failure.

Although TCC has been and will continue to be ***very successful*** in the packaging and marketing HFC-134a refrigerant, service equipment and accessories, we felt the need existed for another alternative refrigerant, especially for the older vehicles. That's why we introduced Freeze 12 to the marketplace.

WHAT IS FREEZE 12?

Freeze 12 is a binary blend of refrigerants consisting of 80% HFC-134a and 20% HCFC-142b. In laboratory and field testing, compatibility with existing CFC-12 A/C systems does not appear to be a major issue. In addition, system flushing and/or component draining to facilitate mineral oil removal is not necessary during conversion. Given the miscibility of mineral oil in HCFC-142b coupled with the mass flow of refrigerant within the system create conditions in which oil return to the compressor is very good.

PERFORMANCE TESTING

In an effort to inform and educate the Mobile A/C Industry at large, the International Mobile Air Conditioning Association (IMACA) cosponsored an independent, third party testing facility to conduct performance testing of Freeze 12 as well as other CFC-12 alternative blend refrigerants being marketed for mobile air conditioning applications. The wind tunnel facilities owned and operated by Moog/Frost Temp in Ft. Worth, TX were used for testing. A neutral observer from IMACA was present for testing and a representative from each refrigerant supplier was invited to attend.

Prior to the performance tests, the vehicles used were inspected to insure proper A/C system operation. Each vehicle was then moved into the wind tunnel and allowed to soak until a temperature of 104°F at 40% relative humidity was attained. Each vehicle underwent testing with CFC-12 first to establish baseline performance. The CFC-12 was then recovered and the conversion procedure published by each refrigerant manufacturer was followed. For Freeze 12, the accumulator drier was changed and replaced with a new drier containing XH-7 desiccant. The primary reason the drier was changed was due to the mileage and age of the vehicle being converted. The vehicle being converted was a 1987 Buick Park Avenue registering 106,000 miles on the odometer. In addition, the instructions for Freeze 12 conversions points out that if a drier has been installed in an A/C system for over 12 months, it should be changed if the system is opened for service. Changing the drier when a system has been exposed to the atmosphere for an

extended period of time is also a good service practice that should be followed regardless of the age of the drier or the type of refrigerant used. Another common practice in the field is a drier changeout due to a compressor failure. It is also important to note that even if the accumulator/filter drier were not changed, on most CFC-12 systems, the XH-5 desiccant likely to be present would be compatible with Freeze 12 due to the absence of HCFC-22 coupled with a protective mineral oil coating around the desiccant. In general, Freeze 12 conversions do not require a drier change as part of a normal conversion, however, in many cases it is recommended due to standard service practices. Three ounces of Polyol ester lubricant were then added to the A/C system. Once again, this is not a requirement for conversion to Freeze 12, however this is a recommended procedure to offset any lubricant lost during refrigerant recovery and as a result of drier changeout. Hose replacement is not required during conversion due to the absence of HCFC-22 in Freeze 12. Unique Freeze 12 fittings were then installed, the system was deep evacuated for 30 minutes and then liquid charged with 10% less Freeze 12 than the original CFC-12 charge called for. A Freeze 12 service label was filled out and placed in the engine compartment of the vehicle. The vehicle was then operated for a period of 1 hour with the A/C controls set on Max A/C and the blower set to high.

As shown in the upper graph of Figure 1, Freeze 12 very closely emulates the performance of CFC-12 in terms of the average interior air temperature of the vehicle. In fact, virtually no performance differential is seen until around 67°F. As seen in the lower graph of Figure 1 which represents the average louver air temperature, Freeze 12 performance mirrors CFC-12 performance down to approximately 47°F. At this point, a small amount of performance differential is seen. On average, the performance of the A/C system in terms of interior air and louver air temperatures was within 3.5°F of what was observed when the system was charged with CFC-12.

As shown in the graph of Figure 2, the high side pressure of the A/C system when operating with Freeze 12 was actually lower than it was with CFC-12. This was due to the presence of the HCFC-142b in Freeze 12. The reduction of discharge pressures would suggest that a reduced load could be seen by the compressor, thus contributing to the durability and reliability of the system in general.

In summary, when the A/C system in this test vehicle was converted from CFC-12 to Freeze 12, efficiency loss in terms of evaporator performance was insignificant. In addition, compression ratios seen at the compressor were effectively reduced by virtue of the HCFC-142b. This strongly suggests that Freeze 12 will contribute to compressor and system durability and reliability.

QUALITY ASSURANCE

As with any refrigerant used in an A/C system, blended or single component, purity and quality are of utmost importance. All refrigerants packaged by TCC including HFC-134a, HCFC-22 and Freeze 12 are randomly sampled and analyzed for purity and composition by a staff chemist and independent laboratories. Product purity and quality are guaranteed by TCC and have been for the past 30 years.

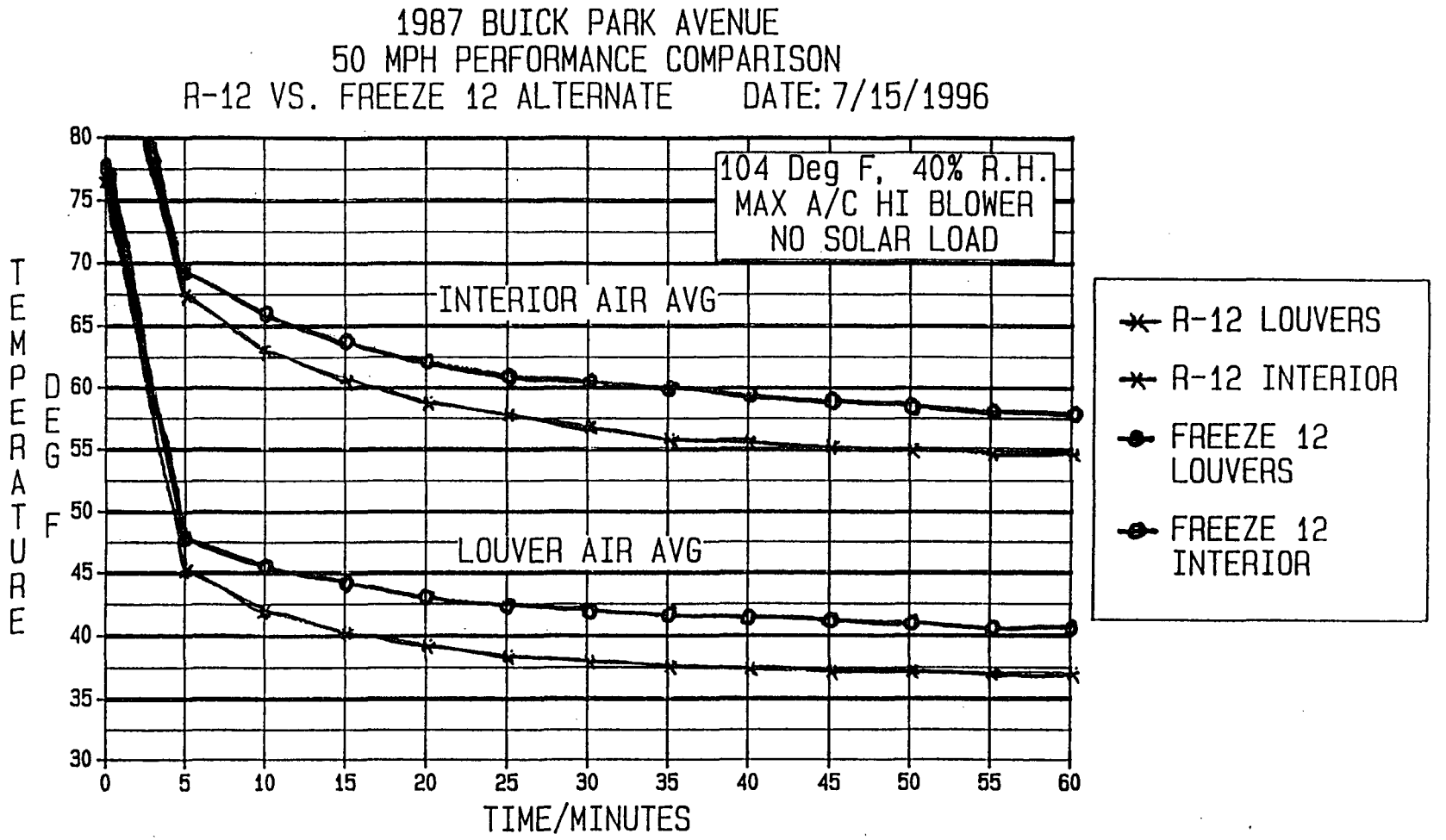
1987 BUICK PARK AVENUE
50 MPH PERFORMANCE COMPARISON
R-12 VS. FREEZE 12 ALTERNATE DATE: 7/15/1996
104 Deg F, 40% R.H.
MAX A/C HI BLOWER
NO SOLAR LOAD
INTERIOR AIR AVG
LOUVER AIR AVG
TEMPERATURE DEG F
80
75
70
65
60
55
50
45
40
35
30
0
5
10
15
20
25
30
35
40
45
50
55
60
TIME/MINUTES
R-12 LOUVERS
R-12 INTERIOR
FREEZE 12 LOUVERS
FREEZE 12 INTERIOR

FIGURE 1

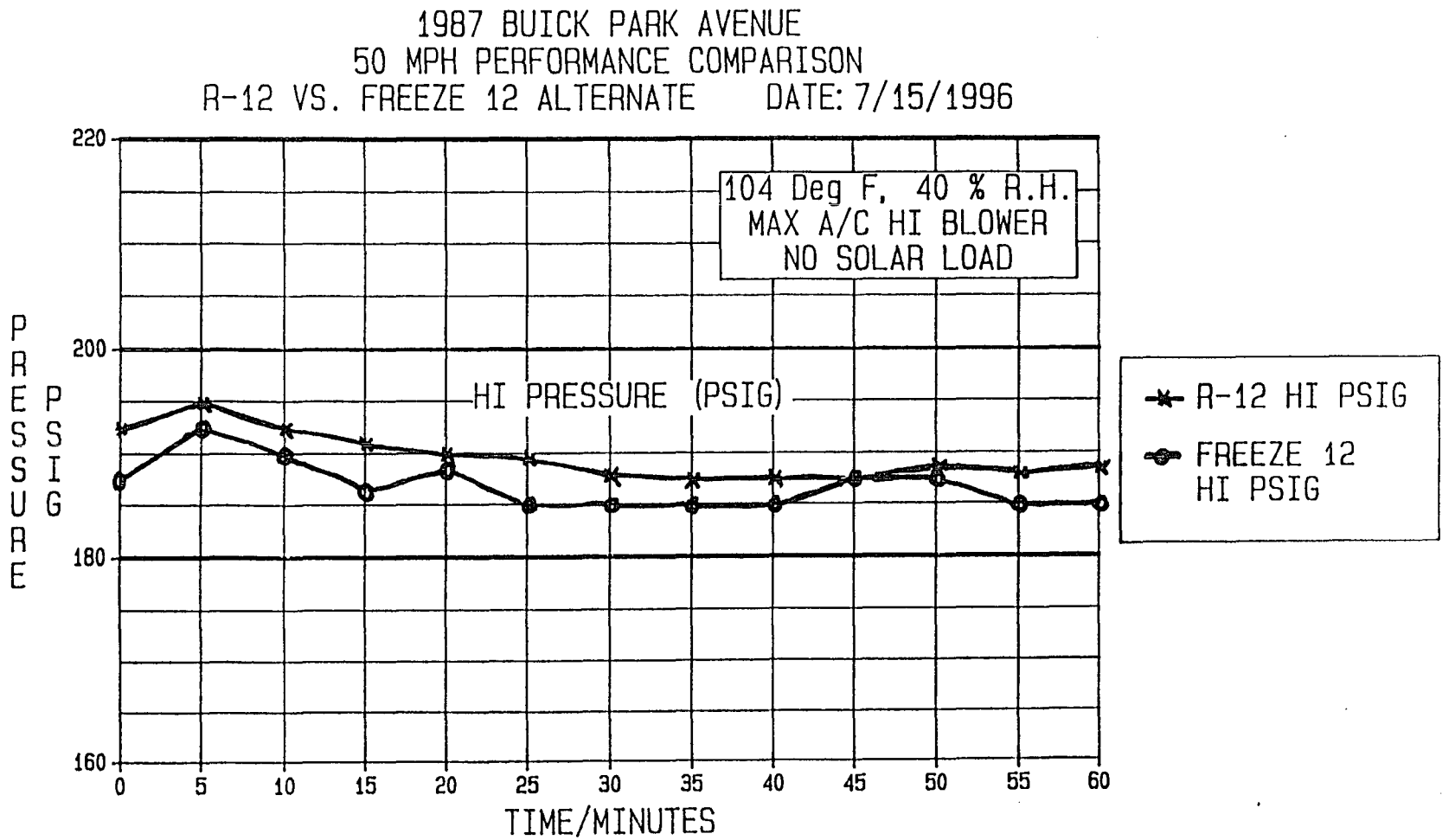
1987 BUICK PARK AVENUE
50 MPH PERFORMANCE COMPARISON
R-12 VS. FREEZE 12 ALTERNATE DATE: 7/15/1996
104 Deg F, 40 % R.H.
MAX A/C HI BLOWER
NO SOLAR LOAD
HI PRESSURE (PSIG)
R-12 HI PSIG
FREEZE 12 HI PSIG
PRESSURE PSIG
220
200
180
160
0
5
10
15
20
25
30
35
40
45
50
55
60
TIME/MINUTES

FIGURE 2

CYLINDER RETURN PROGRAM

Currently, blend refrigerants like Freeze 12 may only be recovered and not recycled. However, a proposed recovery/recycle standard for blends is currently being drafted. In the interim, TCC has established a cylinder return program that will allow a technician to return a cylinder(s) of recovered Freeze 12 back to TCC. Freight both ways will be prepaid by TCC so the technician will not incur any shipping charges.

TCC is also currently negotiating with various refrigerant reclaimers to handle the returned/recovered refrigerant.

A/C COMPONENT WARRANTIES

TCC has submitted samples of Freeze 12 to major A/C component manufacturers for evaluation. As with any new product, including HFC-134a when it was first introduced, evaluation has been conservative. However, TCC is optimistic about the future of component warranty status in light of the extensive, successful bench testing done by TCC. In addition, tens of thousands of successful field conversions have been performed over the last year and a half across the country.

INTERNATIONAL NETWORK OF DISTRIBUTORS

With over 30 years of experience , TCC has packaged and marketed refrigerants and A/C service accessories to the Automotive Aftermarket around the globe. In 1998, a new marketing program will be implemented that will significantly increase the availability of Freeze 12. In addition, all Freeze 12 service labels placed on the vehicle during conversion have a toll-free number preprinted on the label that allow technicians and consumers to access Freeze 12 distributors.

CONCLUSIONS

Freeze 12 is a successful and viable, EPA acceptable alternative to CFC-12 that has already gained significant marketshare based on several factors:

- Good performance can be expected in an A/C system designed for CFC-12
- A reduction of compression ratios that will contribute to compressor and system durability and reliability
- Reduced cost of conversion for many vehicles
- A "no cost" cylinder return program for recovered Freeze 12
- International distribution of Freeze 12 coupled with ongoing, aggressive marketing programs to insure availability

Refrigerant Concentrations in Car Passenger Compartments

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Abstract

Maximum refrigerant concentrations can be predicted from measured charge, leaks, volume and ventilation by simple formulae. Refrigerant 290/600a is a popular 'drop-in' replacement for 12, 134a and 406a in car air conditioners. Physically possible but improbable leaks of R290/600a into the passenger compartment give concentrations above the lower explosive limit for four out of ten Australian cars tested. Simple precautions like placing the expansion valve in the engine bay avoid this.

1 Introduction

A common driver error is failure to see through a misted windscreen. The Australian demister performance standard (FORS 1995) effectively requires fresh air flow into the passenger compartment about 100 L/s. The fresh air required for five occupants with smoking is over 100 L/s. Some manufacturers have increased fresh air well above the minimum for demister performance. Moving the expansion valve into the engine bay (Figure 1) makes a distracting cloud of refrigerant from any passenger compartment failure impossible. These design changes and many others incidentally reduce possible maximum refrigerant concentrations in the passenger compartments of late model cars.

R12 previously used for car air conditioners has a practical limit (BS4434–1995) of 500 g/m^3. The practical limits for the replacements refrigerants 134a, 406a, 290/600a and 600a are 250, 100, 8 and 8 g/m^3, respectively. R290/600a refers here to commercial hydrocarbon mixtures with properties close to those of a 50/50 by mass mixture of propane (R290) and isobutane (R600a). R290/600a is flammable at room temperature and pressure above its lower explosive limit (LEL), 2% by volume, and below its upper explosive limit (UEL), 10%. An Australian code for R290/600a (IAHRA 1996) requires that any physically possible leak not exceed the LEL in the passenger compartment. R600a can reduce the energy consumption and halve the mass of a car air conditioner (Maclaine-cross and Leonardi 1997) but requires equipment redesign.

The maximum concentrations resulting from a typical leak can be calculated for any space and any refrigerant using the formulae in Section 2. The refrigerant charge (Section 3), leakage rate (Section 4) and mixing (Section 5) required are given for car passenger compartments and air conditioners using R290/600a unless specified otherwise. With volume and fresh air flows (Section 6) the peak mean concentrations then calculated (Section 7) suggest recommendations for using R290/600a (Section 8).

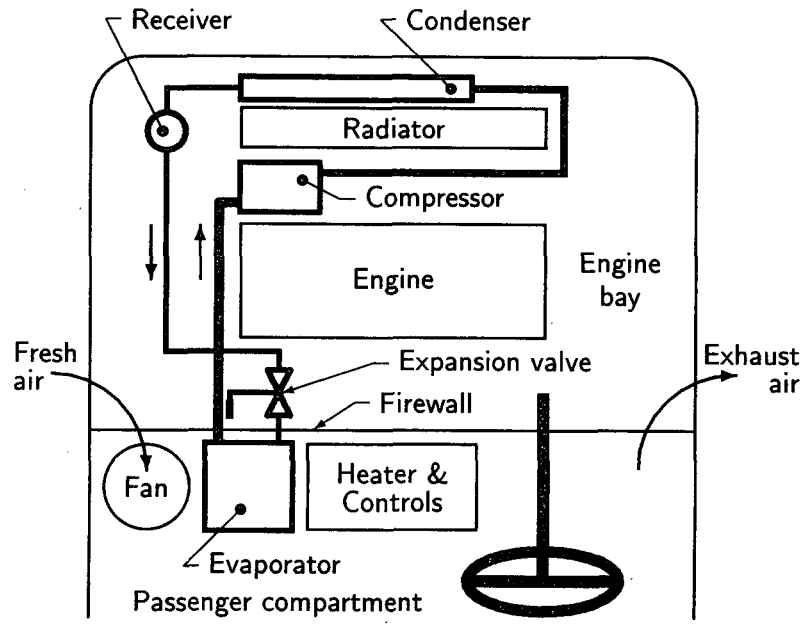

Figure 1: Schematic of car air conditioner with liquid line receiver and expansion valve in engine bay (right hand drive).

2 Calculation of Maximum Concentrations

Figure 2 shows refrigerant leaking into an enclosed ventilated space. Pressure and temperature changes are assumed small compared with absolute except within millimetres of a leak. The volume concentration in exhaust air is assumed close to the mean volume concentration, c.

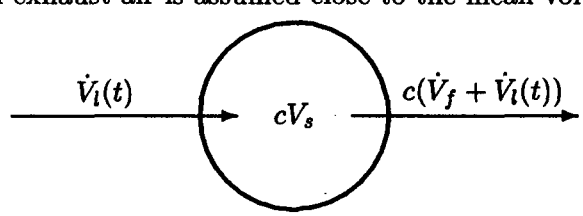

Figure 2: Schematic of refrigerant flows in and out of an enclosed ventilated space.

Conservation of refrigerant mass in the space gives the following ordinary differential equation for the mean volume concentration of refrigerant, c, in the compartment as a function of time, t:

$$V_s \frac{\mathrm{d}c}{\mathrm{d}t} = (1-c)\dot{V}_l(t) - c\dot{V}_f \tag{1}$$

where $\dot{V}_f$ is the volume flow rate of fresh air and V_s is the volume of the space. The volume flow rate of refrigerant into the space, $\dot{V}_l(t)$, is a known function of time depending on initial leakage rate, $\dot{V}_{li}$, and the total volume of the charge, V_c, at the temperature and pressure of the space. The boundary condition used here in solving Equation 1 is $c = 0$ when $t = 0$.

The maximum average concentration of refrigerant in the space, $c_{\max}$, and the time at

which it occurs, $t_{\max}$ are functions of V_c/V_s and $\dot{V}_{li}/\dot{V}_f$ which can be determined by solving Equation 1.

2.1 Constant leak rate

For a leak rate $V_l(t)$ which is constant from $t = 0$ until $t = V_c/\dot{V}_{li}$ at $V_l(t) = V_{li}$, Equation 1 has the exact solutions:

$$t_{\max} = V_c/\dot{V}_{li}$$

$$c_{\max} = \left(1 - \exp\left(-\left(1 + \frac{\dot{V}_f}{\dot{V}_{li}}\right)\frac{V_c}{V_s}\right)\right) / \left(1 + \frac{\dot{V}_f}{\dot{V}_{li}}\right) \tag{2}$$

Slow refrigerant leaks occurring over hours are usually at a constant rate.

2.2 Declining ramp leak rate

A leak rate zero except between $t = 0$ and $t = 2V_c/\dot{V}_{li}$ where $V_l(t) = \dot{V}_{li}(1 - t\dot{V}_{li}/(2V_c))$ is a declining ramp. For $c_{\max} \leq 0.1$, the following formula for $c_{\max}$ is within 1% of exact numerical solutions:

$$t_{\max} = \frac{V_s}{\dot{V}_f} \ln\left(1 + \frac{2V_c\dot{V}_f}{V_s\dot{V}_{li}}\right)$$

$$c_{\max} = 1/\left(1 + \frac{\dot{V}_f}{\dot{V}_{li}} / \left(1 - \ln\left(1 + \frac{2V_c\dot{V}_f}{V_s\dot{V}_{li}}\right) / \frac{2V_c\dot{V}_f}{V_s\dot{V}_{li}}\right)\right) \tag{3}$$

Rapid refrigerant leaks occurring over minutes are usually close to a declining ramp. BS 4434–1995, Clause 1.3.70, defines a *sudden major release* as the majority of the refrigerant charge being released in under five minutes. The initial leakage rate for this to occur, $\dot{V}_{li} = V_c(2 - \sqrt{2})/300$. Figure 3 shows an example of a sudden major release and the resulting concentrations.

3 Refrigerant Charge

The charge is the mass of refrigerant circulating in a system. There is always a minimum charge for satisfactory operation. The system should operate equally well with the initial charge added when the refrigerant is replaced. The minimum charge can be less than 25% of the initial charge in a car air conditioner. The difference between the initial and minimum charges is an allowance for leakage. Often the initial charge of a replacement refrigerant has about the same liquid volume as the R12 it replaces.

When an equal liquid volume of the hydrocarbon mixture R290/600a replaces R12 in a car air conditioner the suction superheat is often 1 K or less. The suction superheat is increased if a lower initial charge is used. A third the mass of the R12 initial charge is used. The large size of R290 and R600a molecules reduces diffusion through elastomers so recharge intervals are similar to R12.

R600a vapour has over four times the specific volume of R12 allowing the minimum charge mass to be more than halved. Its leakage speed is less than half R12 and its molar volume

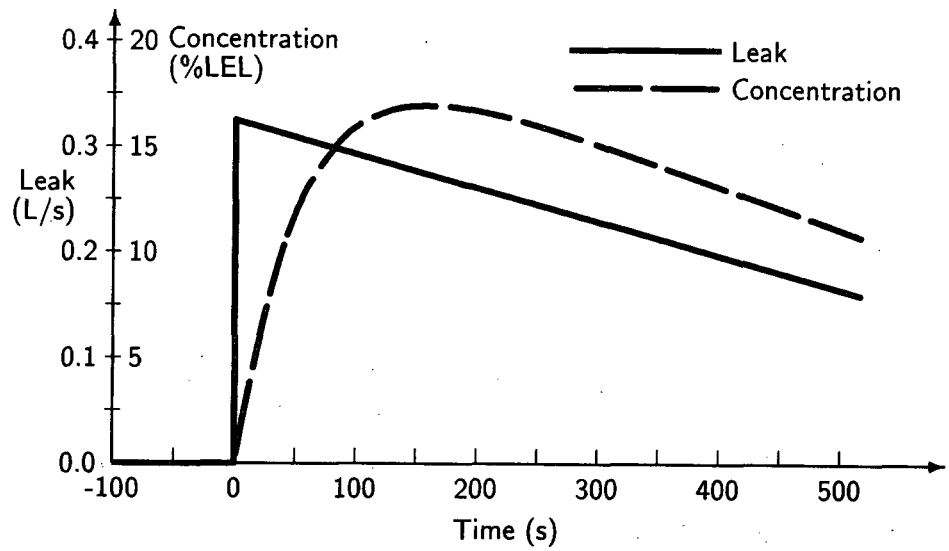

Figure 3: R290/600a flow rate and concentration as a function of time for a sudden major release into the passenger compartment of a 1984 Pulsar with fan on and fresh air vent open (Tables 2 and 4).

is 13% larger (Maclaine-cross and Leonardi 1997) halving the required leakage allowance also. The initial charge mass of an R600a car air conditioner should be less than a fifth of an R12 car conditioner of similar cooling capacity.

4 Leaks and Leakage

Table 1 shows leakages through orifices from a car air conditioner of about 3.5 kW cooling capacity operated on a test bed (Cai 1996). The orifices were on either the liquid line just upstream of the expansion valve or the suction line just downstream of the evaporator and were controlled by a 90° ball valve. After the orifice, a 15 mm inside diameter coil submerged in water at room temperature reheated the R290/600a before weighing in an aluminized polymer bag mounted on electronic scales. The charging cylinder was weighed before and after charging and the differences were close to the mass of refrigerant in the bag at the end of the test confirming measuring accuracy.

The time for 50% of the liquid to escape through the 2 mm orifice was longer than through a 1 mm orifice (Table 1). The refrigerant flashed from the liquid line receiver reducing the density of the fluid flowing through the orifice. Liquid flow rates calculated using line pressure and assuming liquid entering the orifice confirmed this. The poor agreement between predicted and measured maximum vapour flow rates is believed due to errors in orifice dimensions and liquid slugging.

The physically possible failures resulting in loss of refrigerant to the passenger compartment depend on the design of the refrigerant containing components in the compartment:—

1. The structural layer of flexible hoses fatigues with formation of a blister in the sealing layer which then bursts.

Table 1: Measured and predicted leakage of R290/600a through circular orifices from a 3.5 kW car air conditioner operating on a test bed (Cai 1996).

Line with orifice	Liquid		Vapour		
Orifice diameter (mm)	1	2	1	2	3
Refrigerant charged (g)	356	229	271	325	262
Refrigerant collected (g)	321	225	271	330	251
50% collection time (s)	10	11	180	50	25
90% collection time (s)	50	27	370	110	70
Finish of collection (s)	74	34	480	236	100
Peak measured flow (g/s)	15.1	12.3	0.98	6.8	5.1
Predicted peak flow (g/s)	24.6	96.1	0.66	2.7	6.4

2. An O-ring joint is overtightened, stripping the threads without causing an immediate leak.

3. Salt particles cause pinhole corrosion of the evaporator.

The above failures are each known to have occurred at least once in Australia in the last ten years. No examples of the following failures are known but they are believed possible from engineering science:—

4. A fatigue fracture progresses to a crack through the metal.

5. A mercury drop is allowed to rest in the evaporator forming a substantial volume of amalgam with the aluminium which later fractures under normal operating pressures.

For failure of hoses or O-rings in the passenger compartment, I assume frictional, isenthalpic, flashing flow from the receiver to the passenger compartment (Boucher and Alves 1973, Huber *et al.* 1996). For a liquid line with 8 mm internal diameter and a total pressure loss coefficient of 4 the initial flow rate calculated is 250 g/s with compressor on. The experiments of Cai (1996) (Table 1) and Tosovic (1996) suggest the actual flows might be lower. These failures occur when the pressure rises above a critical value so they may occur immediately after the air conditioner is turned off but they do not occur while the engine is off and cooling.

When a corrosion pinhole in an evaporator reaches 0.1 mm the leakage rate is about 10 mg/s when the air conditioner is operating which causes the largest charge (Table 4, 433 g) to leak out in about 12 hours. If the air conditioner is off the leakage rate is about 20 g/s because the pressure in the evaporator doubles. The pinhole has no chance to grow larger since the failed evaporator would certainly be replaced with such a leak rate.

Fatigue fractures grow infinitesimally each stress cycle. Passenger compartment components are subjected to about ten stress cycles an hour. If a vehicle has an operating life of 20,000 hours this is 200,000 cycles of stress. The liquid line is of greatest concern because the same size crack leaks liquid at about 15 times the mass flow rate for vapour. The BS 4434–1995 allowable pressure is 1.7 MPa causing a 9 MPa hoop stress in a 10 mm liquid line. The 500 million cycle fatigue strength for the softest temper of 5152 aluminium tubing alloy is 90 MPa

(ADC 1973). The factor of safety for simple fatigue is more than 10 so no such failures are possible in even soft metal.

With a high stress concentration such as at a scratch, other damage or poor design feature, crack growth and then refrigerant leakage may occur at much lower stresses. Any crack will initially be so small that the leakage could not be detected but eventually the crack grows to 2 mm long. Fracture mechanics (Broek 1982, p. 12–13) predicts that a tensile stress about 400 MPa is required to make such a crack grow catastrophically. The stress at the 1.7 MPa allowable pressure is only 9 MPa so there is a factor of safety over 40 against this possibility.

A 9 MPa uniform stress will open the crack to 0.5 μm width (Broek 1982, eq. 3.59) and at the 1.7 MPa allowable pressure this will leak about 20 mg/s of liquid. When the air conditioner turns off both the gap and pressure are reduced and liquid evaporates leaving only vapour available to leak. Most leaking is with the air conditioner off and at about 1 mg/s of vapour which causes the largest charge to leak out in five days.

5 Mixing

All the refrigerant leaks described in Section 4 are jets submerged initially in air and then later in air/refrigerant mixture. They start at an orifice in the refrigerant circuit which is over 300 mm above the floor at the very front of the passenger compartment. If the fan is on, a leakage into the air duct will all enter the passenger compartment but a leakage outside the air duct may partly or completely leave by the exhaust vent in front of the driver. If the fan is off, all or part of the leakage may leave by the inlet vent as well as the exhaust vent. I assume all leakage mixes into the compartment.

All leaks start with 100% refrigerant concentration which is diluted towards the average concentration in the compartment. The momentum of the jet and natural thermal and density driven convection are always available to drive this mixing. If the compartment is occupied, natural and forced convection from the occupants and usually the fan and motion of the vehicle are also available. For a given orifice, a vapour jet will have a lower mass flow rate and a larger velocity.

Vapour leaks start at close to the velocity of sound in the refrigerant (about 200 m/s for R290/600a). Many measurements have been made of both the velocity and concentration distributions of such jets and the results correlated. Schlichting (1968) summarizes early work and Elias (1996) has applied these and later work to predicting the velocities and concentrations of jets from hydrocarbon refrigerant leaks.

Elias (1996) found a circular R290/600a leak into refrigerant free air had at the 2% LEL contour a velocity everywhere over 1 m/s. On the centreline the velocity was 5.4 m/s at the LEL which was only 200 mm from a 1 mm diameter orifice discharging 1.1 g/s. The flame velocity at the 2% LEL is 0.25 m/s so any flame requires a continuous source of ignition.

Liquid jets are possible only for systems with a liquid line entering the passenger compartment when the system is operating or has very recently operated. The maximum liquid velocity will be about 30 m/s for R290/600a. The liquid flashes to a vapour-liquid mixture at about -30°C . When the mixture has been diluted to the 10% UEL the liquid drops will have evaporated and the density difference is mainly thermal. The mixture falls to the front floor with further mixing and then flows to the rear of the passenger compartment where warming causes it to rise giving a general circulation.

For Razmovski (1994)'s liquid carbon dioxide releases described in Section 6 the sampling point was about the level of the exhaust vent on most of the vehicles. Ten experiments were performed on five Australian cars, half with fan off and vents closed. For all experiments, 80% of the peak concentration was reached within 18 s of opening the valve. On most the peak concentration was reached within 9 s of opening the valve.

The mixing assumption of Section 2 is well satisfied for refrigerant leaks into the passenger compartment.

6 Volume and Fresh Air

Razmovski (1994) and Rajasekariah (1995) measured the volume of and fresh air flows into the passenger compartments of ten Australian cars using carbon dioxide as a tracer. Carbon dioxide was selected as a tracer because its molecular mass is close to propane and instrumentation to measure its concentration was available.

The procedure was to purge, fill and weigh a 2 L fire extinguisher with typically 300 g of liquid carbon dioxide. The extinguisher was fitted with a 90° ball valve with 300 mm handle extension. The car was parked in a sheltered, shaded, outdoor position. The extinguisher was held orifice down by a laboratory stand on the floor in front of the passenger seat and opened by a string passing under the passenger door. The extinguisher orifice was 300 mm above the floor and discharged fully in less than 3 s. The air in the passenger compartment was sampled about 600 mm above the floor, level with the back of the front seats and on the centreline of the vehicle at 0.5 L/minute. The carbon dioxide concentration was measured by a Beckman 865 infrared analyzer outside the passenger compartment. The readings of the analyzer were recorded on a personal computer through a YEW datalogger every 9 s. The maximum wind velocity was always less than 3 m/s.

Table 2 gives the passenger compartment volume and fresh air flows calculated for various configurations of the ten Australian cars tested. The Kingswood and the Volvo air-conditioners did not have a fresh air vent and the Berlina had a fixed fresh air vent.

Razmovski (1994) also used this apparatus with a door switch and electronic timer to measure the loss in concentration when the driver's door was opened fully and closed again quickly without entering the vehicle. Table 3 shows this concentration loss is significant for many vehicles.

7 Peak Concentrations

Table 4 gives peak mean concentrations for leaks of R290/600a calculated using Equations 2 and 3 and converted to %LEL. The ratio of charge to volume in column 5 is always higher than the last four columns. The multipliers to convert column 5 to a percentage of practical limit (BS4434-1995) are 0.24, 0.44 and 0.97 for refrigerants 12, 134a and 406a respectively used on the same car. For a new design, using R600a the charge to volume ratios can be less than half those in column 5.

Column 6 of Table 4 gives the concentrations resulting from a sudden major release (Section 2.2). BS 4434–1995 requires for other applications that the practical limit not be exceeded. The practical limit is 20% of the LEL for R290/600a and the seven cars manufactured after

Table 2: Measured passenger compartment volume and total fresh air flows for ten Australian passenger cars (Razmovski 1994, Rajasekariah 1995). The first three configurations have all windows closed and the last three have the fan operating at full flow. The third (F.V.) has the fresh air vent open and the last (F.W.) also has the driver's window open.

Model	Year	Vol. m^3	Fresh air (L/s)			
				Fan	F.V.	F.W.
Kingswood	1970	5.81	1.05	2.52	2.52	
Volvo	1978	6.48	4.00	20.8	22.0	1363
Commodore	1979	3.81	5.78		85.0	
Pulsar	1984	4.16	0.61	20.2	77.4	
Corolla	1985	5.68	3.00	20.0	149.7	262.2
Falcon	1987	4.44	38.03	164.0	134.5	151.2
Laser	1988	3.48	1.42	4.56	85.1	41.0
Berlina	1989	4.36	2.95	173.0	173.0	
Magna	1989	6.12	6.00	37.0	100.7	987
Astron	1989	5.50	50.0	143.0	136.0	312

Table 3: Loss in tracer concentration in the passenger compartment when driver's door briefly opened fully and closed with fan off and vent closed (Razmovski 1994).

Model name	King.	Comm.	Pulsar	Laser	Berlina
Year of manufacture	1970	1979	1984	1988	1989
Time door open (s)	5.70	3.60	3.27	3.60	3.70
Tracer conc. loss (%)	10.3	33.6	29.8	21.8	19.7

Table 4: Expansion valve position, initial charge of R290/600a, ratio of charge to volume and peak average concentration in the passenger compartments of ten Australian cars as a percentage of the lower explosion limit (LEL) for four release scenarios. P=in passenger compartment, E=in engine bay.

Leak type					Sudden	Worst		
Fan is					on			off
Vent is					open		closed	
Model	Year	Valve Pos.	Charge g	Charge %LEL	Peak concentration %LEL			
Kingswood	1970	P	280	120	92	118	118	44
Volvo	1978	P	367	141	46	137	137	13
Commodore	1979	E	420	276	21	0.6		9
Pulsar	1984	E	333	200	18	0.6	3	74
Corolla	1985	P	233	103	7	98	100	17
Falcon	1987	E	433	244	14	0.4	0.3	1.3
Laser	1988	P	233	167	12	157	162	35
Berlina	1989	E	367	210	9	0.3	0.3	17
Magna	1989	P	233	95	9	92	93	8
Astron	1989	P	283	129	9	121	121	1.0

1980 meet it. Values for refrigerants 12, 134a and 406a are not given but they exceed their practical limits for none of these cars.

The last three columns of Table 4 use the worst leak physically possible for the design and operation condition described in Section 4. IAHRA (1996) requires that with fan on and vent open the LEL not be exceeded and column 7 shows six of the vehicles satisfy this. Column 8 shows although closing the fresh air vent where one exists increases the peak concentration, the same cars still satisfy the IAHRA requirement except no fresh air measurement was made for the Commodore.

Column 9 is for leakage when the vehicle is unoccupied with engine and air conditioner off. Any instantaneous complete fracture must result from a pressure increase which may occur immediately after the ignition is turned off. Even if the occupant ignores the cloud, leaving the car drops the concentration (Table 3) making the slower leaks worse. None of the ten cars exceed the LEL.

8 Conclusion

Manufacturers of car air conditioners for R290/600a or R600a should comply with the requirements of BS 4434–1995 for stationary systems. In particular, there should be no screw fittings or elastomer hoses containing refrigerant in the passenger compartment. They should minimize the design initial charge.

An R290/600a retrofitter should for the passenger compartment replace damaged mountings or screw fittings and replace elastomer hoses with metal extensions or add IAHRA (1996)

safety valves. Do not retrofit cars without fresh and exhaust air vents. The initial charge should not exceed either 400 g or a third the charge recommended for R12. Do not use mercury-in-glass thermometers.

References

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REFRIGERANT BLENDS - TECHNICAL CONSIDERATIONS OF RECOVERY AND RECYCLE OF REFRIGERANTS IN MOBILE AIR CONDITIONING SYSTEMS

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ABSTRACT

The USA Clean Air Act requires recovery of all replacement refrigerants including refrigerant blends. There are no specifications that identify requirements for recovery or recycle equipment for these refrigerant blends. This paper addresses potential requirements as they relate to present practices and identifies the technical considerations of recovery and recycle of refrigerant blends.

INTRODUCTION:

The Montreal Protocol, the USA Clean Air Act, and subsequent EPA regulations are intended to preserve the earth's protective ozone layer. This has had an impact on the mobile air conditioning system market, from automobile manufacturers to the service technicians and individual automobile owners since R-12 production has been discontinued in the USA. It is necessary to implement all possible actions to preserve usable amounts of R-12 to service existing equipment. As supplies diminish, alternatives will compete for the replacement market. New refrigerants have been developed to replace R-12 in mobile air conditioning systems and are available in the marketplace. Some of these alternatives are known as refrigerant blends. Since refrigerants are required to be recovered and the mobile air conditioning market is accustomed to recycle refrigerants, it is necessary to identify the requirements applicable to recovery and, if possible, recycling of the refrigerant blends currently approved for the mobile air conditioning market system. This is intended to assist in the development of suitable recovery or recycle equipment.

BACKGROUND:

Refrigerant 12 (R-12) was the only refrigerant traditionally used in mobile air conditioning system applications. As a result of years of experience the properties of the gas and the cooling systems are well understood. Service procedures for R-12 are well defined and, for the most part, uniform from vehicle to vehicle. Risks and hazards are well understood and integrated into the design, operational and service procedures.

When researching alternate refrigerants for new vehicles, required due to the banning of the production of R-12, one fundamental consideration was to develop an alternative that would not create significant differences in current equipment or procedures and where an equivalent level of field experience could be created and feedback developed to influence design, operation and service of future systems. The choice was made by auto manufacturers early once they understand that R-12 would be banned and when there were few possible alternative refrigerant choices. Refrigerant R-134a seemed to meet most of the fundamental criteria for an alternative. However, it was necessary to change the type of oil used, to modify some system components and to revise the system design to accommodate the slight difference of performance of R-134a. Prior to 1995 there were two possible refrigerants being used by OEM's in vehicles, R-134a and R-12. After 1995, R-12 would be available only from existing stockpiles or in recycled form and all new cars used R-134a. It was, therefore, necessary to identify the refrigerant that was in a vehicle air conditioning system and develop methods to minimize and avoid, if possible, the mixing of the two chemicals.

In order to preserve supplies of R-12 as long as possible, to service existing vehicles, it is the intent of Section 609 of the Clean Air Act to recycle R-12 used in mobile air conditioning systems.

SAE STANDARDS:

SAE Standards were developed to address system design recycle/recovery procedures and service procedures.

The basic objectives of these standards are:

1) recycle existing supplies of R-12 as long as possible and recycle R-134a in a similar manner,
2) to fully qualify any new alternate refrigerant,
3) be sure that a service technician would know what refrigerant was in the vehicle, and
4) provide design features that would help to avoid accidental mixing of different refrigerant gasses and thereby avoid putting the wrong refrigerant gas into a vehicle.

Other major points in these standards are:

1) The alternate refrigerant is to be nonflammable when tested in a 66°C ambient (Ref: Clause 5.2 of SAE Standard J1657). Fractionation shall not result in flammability of the refrigerant.
2) The refrigerant system is to be fitted with unique fittings for service hose connections when R-134a is used as the alternate. (Other alternative refrigerants have similar rules specified by the EPA.)
3) The refrigerant system is to be marked to identify that the refrigerant R-134a is used as the alternate. (Other alternate refrigerants have similar rules specified by the EPA.)
4) The toxicity of a refrigerant is covered by reference to the US EPA's Chemical Inventory list as required by the Toxic Substance Control Act (TSCA).
5) The requirements for purity of the recycled refrigerant (R-12 and R-134a) are specified.
6) The refrigerant shall be compatible with the materials used in the air conditioning system (SAEJ1662).
7) Vehicle performance tests are conducted with the retrofitted refrigerant to confirm that the system cooling capacity is equivalent to the original R-12 system.

SNAP:

SNAP (Significant New Alternative Program) is the U.S. EPA's program for evaluating alternative refrigerant. SNAP concepts for vehicle air conditioning systems, that are retrofitted with a new refrigerant, include the following:

1. The refrigerant system is to be marked to identify the refrigerant.
2. The refrigerant system is to be fitted with unique fittings for service hose connections.

The reasons for these requirements relate to Section 609 of the U.S. Clean Air Act of 1990. The requirements were developed to help avoid mixing different refrigerant gasses, particularly with R-12.

REGULATIONS:

For mobile air conditioning system service technicians, the critical points in the Clean Air Act of 1990 and subsequent EPA regulations are:

- The regulated refrigerant gasses shall not be vented to the atmosphere (i.e. CFC's and HCFC's).
- Any CFC refrigerant gasses must be recovered and shall not be vented to the atmosphere.
- The regulations support the SAE standards principles.
- Any alternate refrigerants must be accepted by the EPA under SNAP (Significant New Alternative Program), and to obtain SNAP acceptance, the following criteria is evaluated:

a) The refrigerant must be nonflammable or the risk of flammability fully qualified.
b) The health effects and the environmental impact are evaluated for compliance with the Clean Air Act by the EPA.
c) The safety aspects of the refrigerant are considered.
d) Retrofitted vehicle air conditioning systems shall be marked to identify the refrigerant.
e) The retrofitted system shall be provided with unique service fittings.
f) The refrigerant shall be recovered and could be subsequently reclaimed or recycled. It shall not be vented to the atmosphere.

SERVICE OF MOBILE AIR CONDITIONING SYSTEMS:

From the perspective of the 1996-1997 time frame, there is a need to provide service for mobile air conditioning systems that require recharge or repair and that have been designed for Refrigerant R-12. When determining how to best service these systems, the following options are available:

- Use R-12 available from stockpiled or recycled supplies or from a reclaimer.
- Install a retrofit kit developed by the vehicle manufacturer using an EPA acceptable refrigerant. Presently many, but not all, vehicles can be retrofitted by a procedure specified by the vehicle manufacturer using Refrigerant 134a.
- Use some other method not necessarily approved by the vehicle manufacturer, but is acceptable to the EPA and the customer.
- Do not repair the vehicle's air conditioning system.

Decision Tree No. 1 is based on conditions that have been reported in the mobile air conditioning system market and illustrates options with information related to each other.

SUBSTITUTES:

The EPA has "accepted" nine substitutes for vehicle air conditioning systems (as of October 1996). One of these is R-134a which is being used in all new vehicle air conditioning designs. All others are blends of different refrigerant gasses designed to replace R-12 in a mobile air conditioning system with

a minimum amount of system changes and to match, as close as possible, the characteristics of Refrigerant-12.

The following identifies characteristics of R-12 systems that are considered important to match.

- Pressure-Temperature Characteristics
- Material Compatibility Characteristics
- Refrigerant Containment System Compatibility
- Oil Compatibility

RECOVERY/RECYCLE OF MOBILE AIR CONDITIONING REFRIGERANT:

These same items are also major considerations in the ability to recover or recycle blended refrigerants that could be used in a vehicle. They affect the design of the recovery or recycle equipment and the ability of that equipment to operate safely and to provide a usable recycled refrigerant.

Decision Tree No. 2 illustrates the current options identified in the mobile air conditioning system market when a blend is to be considered for removal from a vehicle.

REFRIGERANT BLEND RECOVERY/RECYCLE:

For blends, all of the options illustrated may not be technically feasible.

Diagram 1 is a system requirement/functional diagram of a possible "universal" mobile air conditioning refrigerant blend recovery and/or recycle machine. It is expected for the purposes of this discussion that the refrigerant would be recovered first and, if recycling can occur, it would be another step after recovery.

The objective of the diagram is to identify critical parameters related to what could occur in the field and define the system requirements to address potential safety and environmental risks. When these items are understood, suitable equipment designs capable of handling the functions intended could be produced on a cost effective basis.

RECOVERY AND RECYCLE EQUIPMENT:

The most desirable piece of equipment for service would be a machine that could collect any and all refrigerants that are expected to be in a vehicle and, after separating, cleaning and properly remixing the blend, deliver a particular recycled refrigerant for return to the vehicle. The particular recycled refrigerant (blend or single component refrigerant) would be specified by the operator as the one suitable for that vehicle based on the markings and fittings. However, the technologies related to chemical identification, chemical separation and the recovery/recycle process have not advanced sufficiently to permit a cost effective solution. At this time, the most likely destination for an unknown mixture of chemicals in a recovery tank is destruction.

RECOVERY EQUIPMENT:

The most practical type of equipment would be a recovery machine that could recover any and all refrigerants that are expected to be in a vehicle and recover them into a tank

identified for leaving the service site for destruction or possible reclamation. Focus is presently on developing the initial requirements for this type of equipment. A future option would be to consider the parameters applicable to recycle equipment.

SINGLE REFRIGERANT BLEND RECOVERY EQUIPMENT:

A recovery machine would be designed to process one particular blend. In which case, it would be necessary to know that the refrigerant in the vehicle is the one that the machine is designed to recover, that the refrigerant recovered is the refrigerant intended, and that refrigerant is identified on the container or is returned to a vehicle with the proper fittings and markings.

REQUIREMENTS, RECOVERY EQUIPMENT:

In developing the requirements, the recovery equipment will need to adequately process any possible mix of refrigerants. The following are considered.

a. What design/pressure and safety factor should be applied to the pressure containing parts.
b. The equipment materials that are in contact with the refrigerants shall be compatible with all the possible chemicals.
c. The performance of the oil separator shall be specified and confirmed.
d. The fill percentage of the refrigerant containment tank shall be properly specified and limited by equipment design, to avoid the risk of a tank explosion.
e. The possible flammable aspect of the refrigerant gasses should be addressed with respect to the risk of a hazard to a service facility if flammable gasses could leak from a vehicle, the recovery equipment, or the tank and hoses.
f. The material compatibility of hoses and seals shall be specified to meet the current compatibility requirements for each refrigerant component.
g. The hoses will be permanently supplied with the equipment and one will be provided for each type of fitting associated with an "acceptable" blend. (Note: The EPA may rule on the use of adapters. Adapters are not currently permitted.)
h. There may be other items critical to system designs, usage, OEM concerns, etc.

The chemicals that could be present shall be only those known to be in vehicles today and those contained in refrigerants or refrigerant blends that have been accepted by the EPA. The oil types are those known to be used in vehicles at the present time. The moisture levels are related to the oil and refrigerant characteristics. Particulates are required to be filtered out at the same level as is presently specified for R-12 and R-134a. Air contamination is expected to be at the same level being experienced today for a specific refrigerant. The requirements for oil separation are similar to those for R-12 and R-134a, but must include oils known to be in a mobile air conditioning system.

Because several flammable substances could be present (R-290, R-600, R-600a, R-142b are classified as flammable refrigerants) the equipment shall be designed for use in Class 1, Division 2 locations. Because the equipment processes possible flammable gasses, but these gasses are not normally present in the atmosphere, the location where these machines will be used must be a suitable Class 1, Division 2 location.

The recovery tank shall be identified as a container of unknown refrigerant (colored gray with a yellow top). Because the tank is not identified and the equipment may be capable of handling any possible mixture of chemicals that may be recovered (as noted in Diagram 1), there is no need to identify by test what was in the vehicle, what is going into the recovery equipment or what comes out of the recovery equipment. The test points noted in Diagram No. 1 would not apply.

REQUIREMENTS, RECOVERY FOR SPECIFIC BLEND EQUIPMENT:

In this case, the refrigerant in the vehicle can be identified by the markings and fittings on the vehicle. The refrigerants may need to be identified by a suitable refrigerant identifier (Test Point A). It would also be necessary to identify by test that the refrigerant in the recovered tank is the refrigerant specified (Test Point B).

REQUIREMENTS, RECYCLE EQUIPMENT:

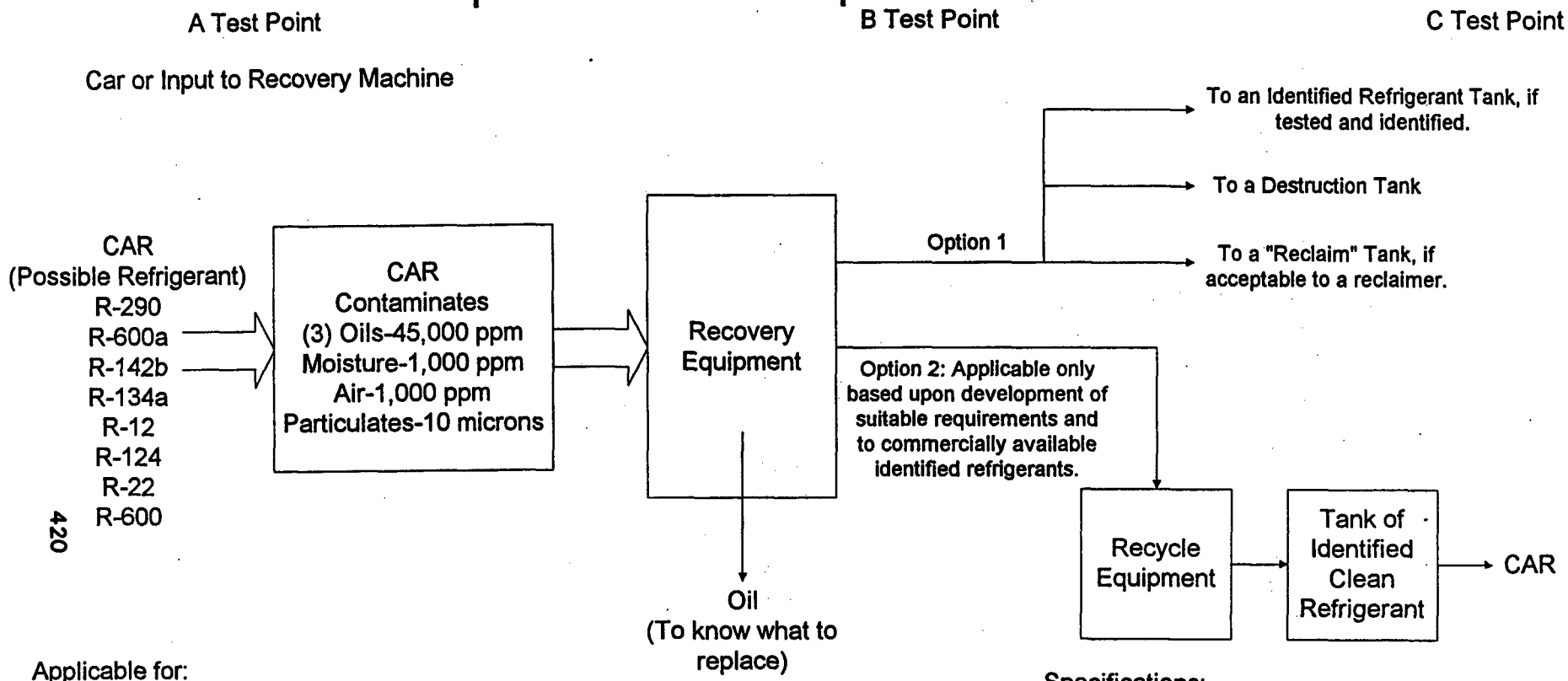
For recycle equipment, the basic function would start just before Test Point B. It may be possible to recycle a known refrigerant that is tested at Test Point B and know that the resultant refrigerant from the recycle machine is an acceptable refrigerant for use in the mobile air conditioning system. However, tests at one or the other Test Points (B or C) would be necessary to fully qualify what is returned to the vehicle.

SUMMARY:

The Montreal Protocol is intended to preserve the earth's stratospheric ozone layer, and protect the health of all the earth's occupants. The Protocol and subsequent USA legislation and regulations are intended to preserve the ozone layer and have eliminated production of R-12. To provide cost effective service for using R-12 in air conditioning systems, it is necessary to implement all actions possible to preserve the present supply of R-12 through recycling and recovery. In addition, suitable alternatives are being developed. The USA regulations require recovery of all refrigerants and most of the mobile air conditioning system service technicians are accustomed to recycling. Since these are alternative refrigerant blends available in the marketplace, it is necessary to identify the requirements applicable to recovery and/or recycling of these blends to assist manufacturers in developing suitable equipment.

The requirements for such equipment, along with the technical rationale, and the present status of the market have been identified.

Diagram No. 1
Requirement Concept Schematic



Applicable for:
Components of "accepted" EPA blends and only chemicals known to be in mobile air conditioner system.

High contaminate levels that could be in the refrigerant and in the system.

(3) Oils
Mineral Oil
Polyalkylene glycol (PAG) Oil
Polyol ester (POE) Oil

Specifications:
_% of identified blend components
___ oil
___ moisture
___ air
___ particulates
(to be developed)

EPA "ACCEPTED" blend refrigerant, also accepted by equipment owner, service facility or other responsible organization.

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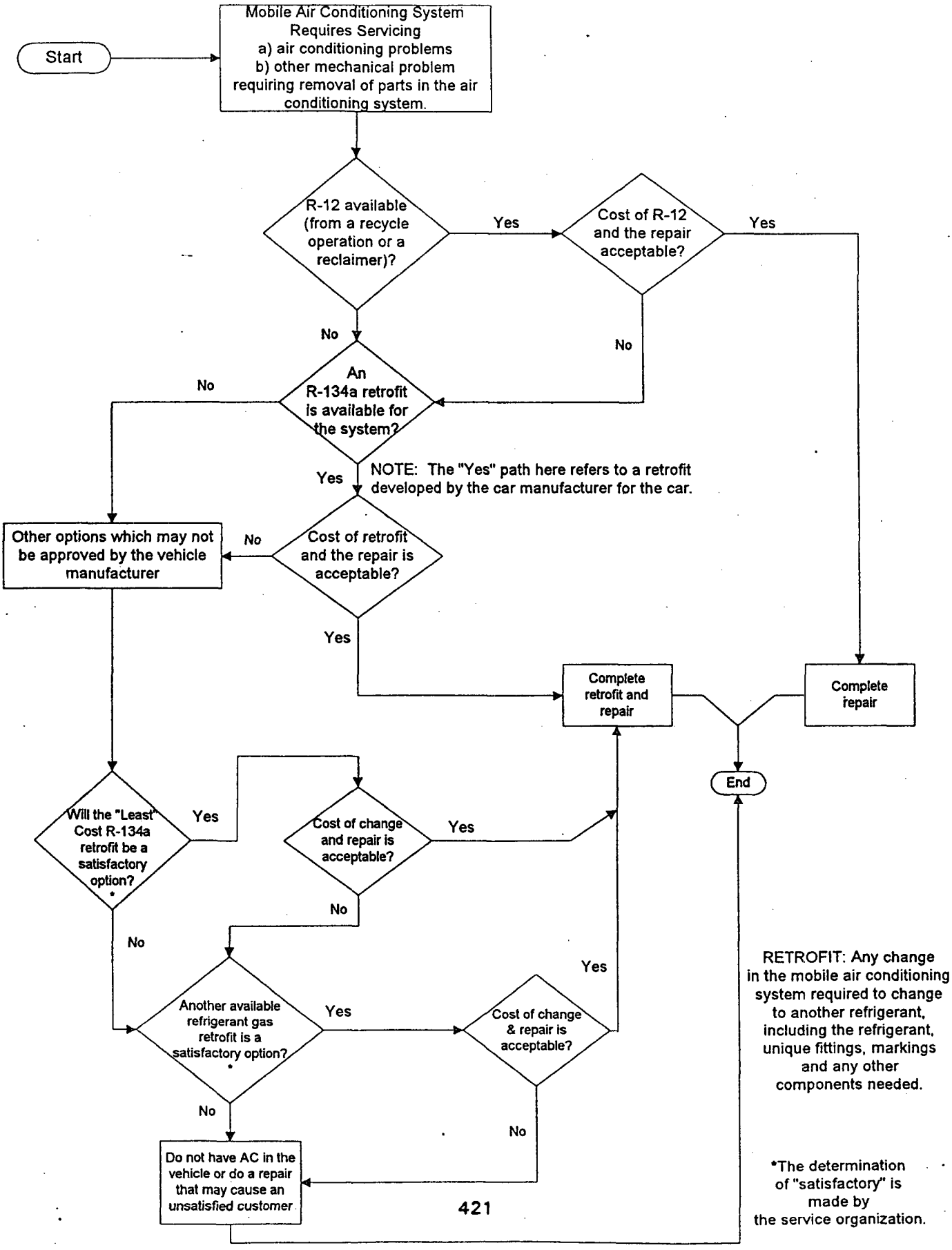
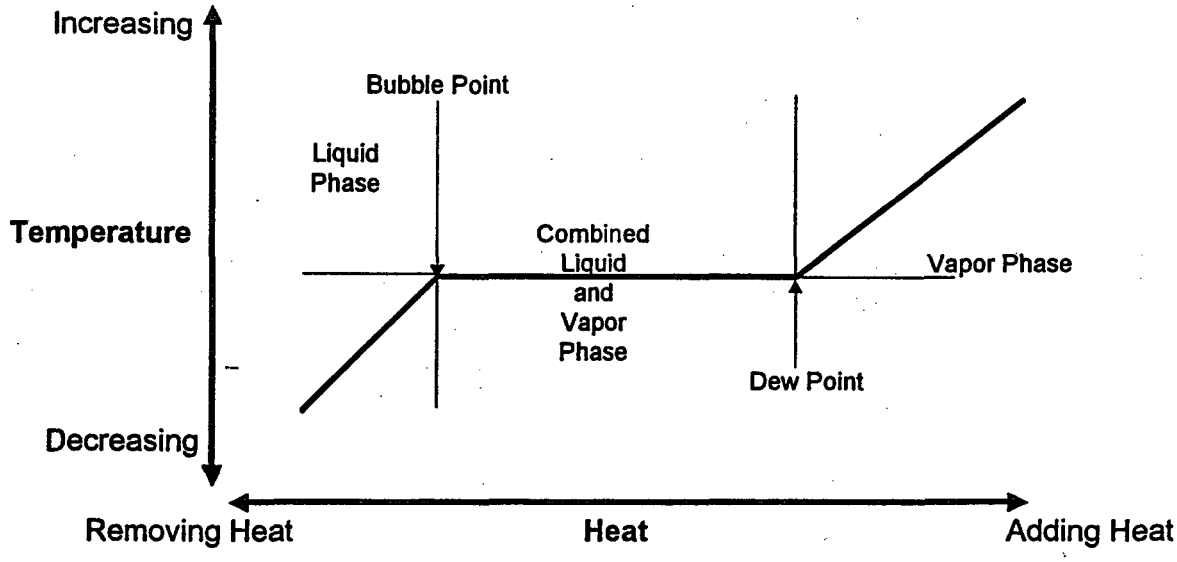
DECISION TREE NO. 1, CAR AC SERVICING

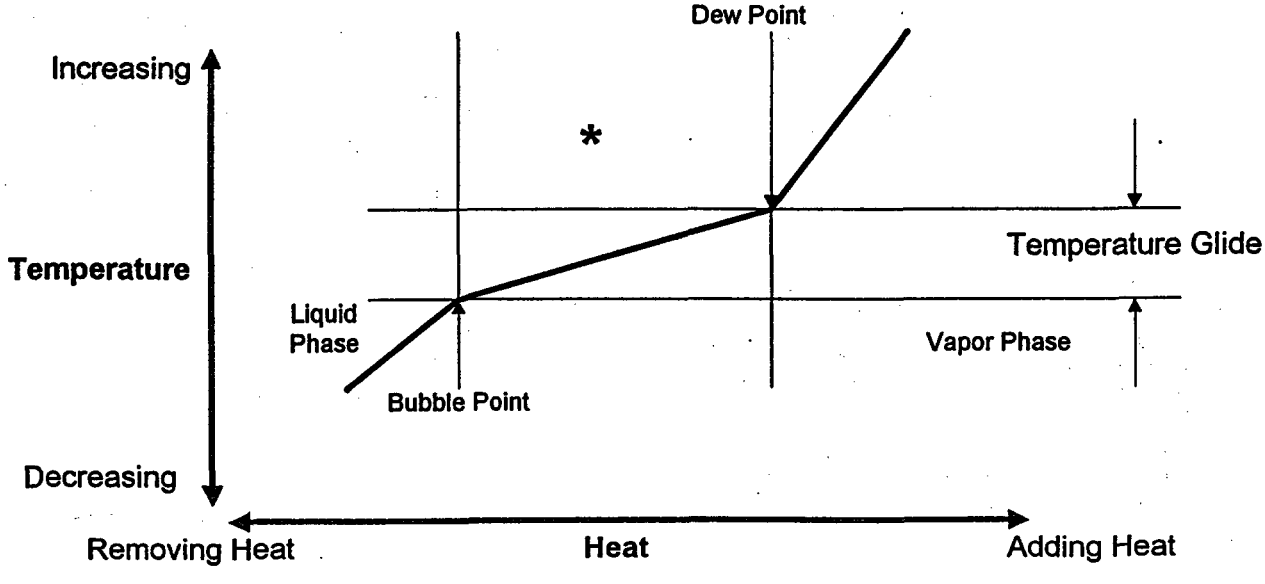


GRAPH 1 SINGLE CHEMICAL



Below the bubble point temperature, only liquid exists. At the bubble point, the liquid begins to evaporate (adding heat). At the dew point, the vapor begins to condense (removing heat) .Above the dew point, only vapor exists. The dew point and the bubble point occur at the same vapor or liquid temperature for a single chemical, but may not for a blend.

GRAPH 2 BLENDED CHEMICAL



* Combined liquid and vapor phase but the composition percentages of the component chemicals will be different than the "as composed" blend composition and the vapor composition and the liquid composition will be different..

NOTE: These graphs assume that the pressure is constant. Similar graphs can be made that assume that the temperautre is held constant (replace the word "temperature" with "pressure" and note a "pressure glide"). Changing both the temperature and the pressure causes a more complex interaction.

CFC Collection Systems for Refrigerant and Insulation Foam and CFC Decomposition System

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0. Summary

For the purpose of the Ozone Layer Protection, it is important technology to collect and decompose the existing CFCs contained in the several kinds of equipment. In order to achieve effective collection and decomposition of these CFCs, Hitachi focused on CFCs contained in household refrigerators and has developed and commercialized three systems which are the collecting system for refrigerant CFC, for blowing agent CFC and a decomposition system for collected CFCs.

These systems were installed in a pilot plant for recovering CFCs of the Association for Home Appliances in Japan (AEHA).

1. Introduction

Ozone Layer protection is an urgent global Issue and the Montreal Protocol was agreed upon and amended to phase out Ozone Depleting Substances. For the purpose of actual reduction of the atmospheric chlorine concentration, it is important to collect and decompose these substances since the Montreal Protocol only controls future production of these ODCs and there has been large amount of accumulation of ODCs produced in the past.

Taking account of this background, the most effective way is to collect and decompose ODCs. Therefore, series of systems were developed mainly focusing on the collection and decomposition of CFCs used in household refrigerators.

Old household refrigerators used CFCs as a refrigerant and as a blowing agent for the thermal insulator. Thus, the collection system for the refrigerant CFC, the collection system for blowing agent CFC and the decomposition system for these CFCs are well suited for disposed refrigerators.

2. Collecting System for Refrigerant

The system is composed of three units which are the drilling unit, the separating unit and the recovery unit. Basic system structure is shown in Figure 1.

At an ambient temperature of 20 degrees celsius, approximately 80% of refrigerant is dissolved in lubricating oil. When collection is made of CFC in gaseous phase, it will take more time because the CFC must evaporate from the dissolved oil. Therefore, it is important to collect dissolved CFC in oil. Firstly, a disposed refrigerator is conveyed to the drilling unit. The unit drills a hole in each compressor casing to collect lubricating oil including dissolved CFC.

The separating unit is connected to the drilling unit with high pressure tubing and separates the dissolved CFC from lubricating oil.

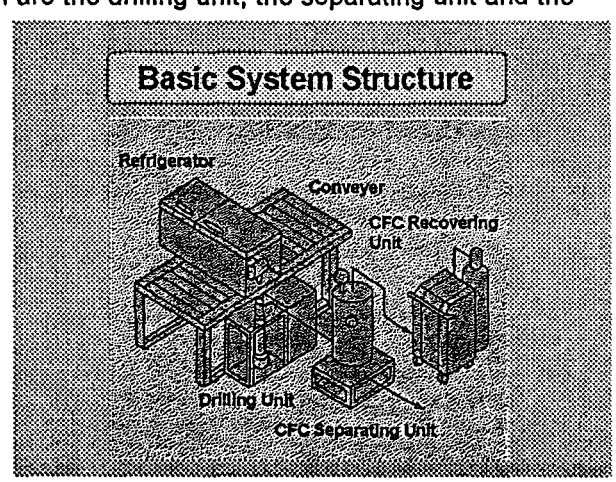

Figure 1

Several features are added in this unit for faster separation of CFC from lubricating oil such as evacuation, heating and agitation.

Lubricating oil is drained and CFC gas is collected by the Recovery unit. If there, the existing Recovery unit may also be used for the collection.

Table 1 shows the specification of the system. The system is compact and easy to transport by small truck and to assemble by connecting three units.

This system enables to achieve higher collection rate and faster collection speed of the refrigerant CFC.

CFC Collecting System Specifications

Capacity:	3 minutes/Refrigerator except the time for mounting
Utility:	Electricity Dried Air 5kg/cm^2
Dimensions:	2,000mm(W) 4,000mm(L) 2,000mm(H)

Table 1

3. Collecting System for Insulation Foam

Two kinds of CFCs are used in household refrigerators, one is CFC-12 and other is CFC-11 as shown in Figure 2. Approximately, 500g of CFC-11 are contained in the thermal insulator. This content is 3 times more than that of refrigerant CFC-12 which is about 150g. This insulator is located between outer steel panel and inner plastics panel as cross section shows. It has very a fine cell structure of polyurethane foam. A magnified picture of the cell structure is shown in the right above of Figure 2. CFC-11 is contained in each cell of the insulating foam. Thus, it is necessary to recover CFC-11 from each cell.

For this recovery, Figure 3 shows the schematic diagram of how CFCs are collected. At the first stage, refrigerant CFC-12 is collected using the system explained above. Next, after removal of the compressor, refrigerator is conveyed to a primary crusher. During primary crushing, cells of polyurethane are broken and CFC-11 is emitted, but the concentration of CFC-11 is not high and a low concentration recovery system collects it.

Next, the refrigerator is crushed at a secondary crusher. At this stage, crushed materials are separated into metal and plastics. After this separation, plastics and light metals are sent to polyurethane tilting air sorter, and separated into polyurethane and other plastics. Separated polyurethane is sent to a fine crusher and each cell of the polyurethane is destroyed. During fine crushing, emitted CFC-11 is collected and crushed polyurethane is compacted to a disk.

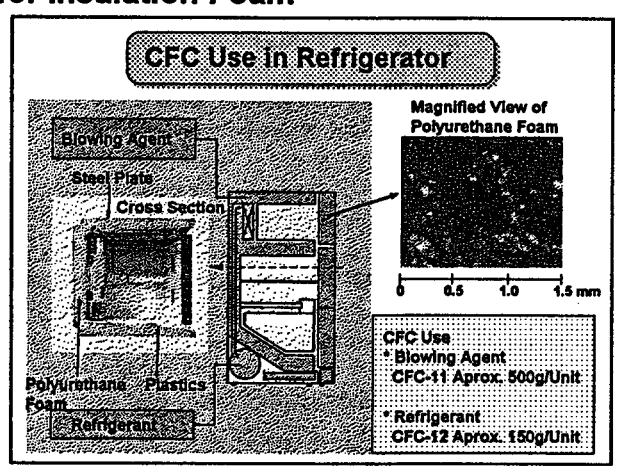

Figure 2

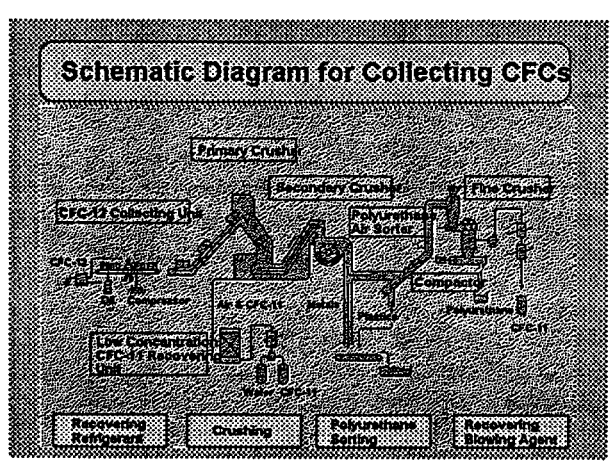

Figure 3

This recovery system is installed at a pilot plant of the Association for Electric Home Appliances Japan (AEHA) in 1996. Figure 4 shows the installed
plant. More particularly, it shows the fine crushing stage of the system.
This system is capable of 3 tons an hour, or approximately, 50 refrigerators can be processed in an hour.

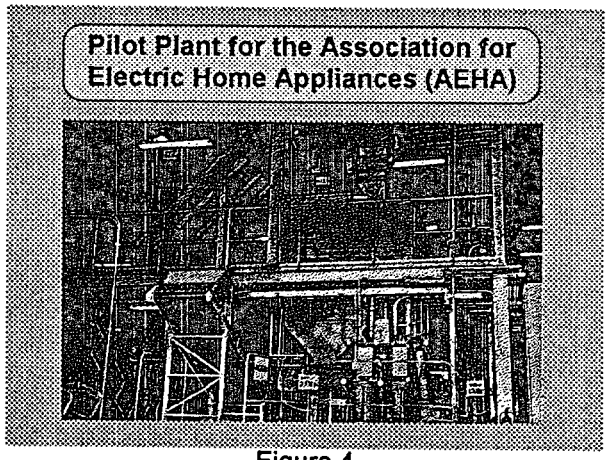

Figure 4

4. CFC Decomposition System

Several approach have been proposed for the decomposition of CFCs such as incineration, plasma decomposition, etc. CFCs are stable chemicals and require a temperature higher than 1,000 degree celsius. Considering energy efficiency for decomposition, Hitachi developed an effective catalyst and transportable decomposition system.

4.1 CFC Decomposition Process

The chemical reaction formula for decomposition of CFC-12 is shown in Table 2. CFC-12 reacts with water and creates hydrogen fluoride, hydrogen chloride and carbon dioxide. In this decomposition process the catalyst plays important role. The first mentioned two chemicals are strong acids and it is necessary to neutralize them.

The second formula shows the neutralization reaction with calcium hydro-oxides. Resulting calcium fluoride and calcium chloride can be used as raw materials

The third formula explains the whole decomposition reaction of CFC-12.

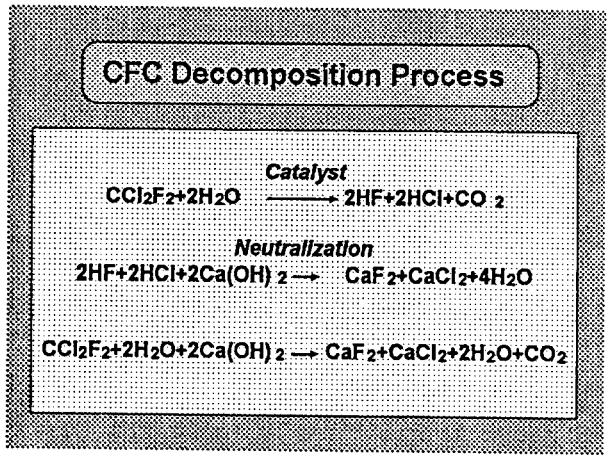

Table 2

4.2 Characteristics of Catalyst

Applying the newly developed catalyst, characteristics with temperature versus CFC-12 decomposition rate are shown in figure 5. This catalyst is capable of decomposing 60% of the CFCs at 600 degree celsius.
99.99% of CFC-12 can be decomposed at 400 degree celsius. Lower temperature decomposition may result in longer life of the catalyst and system as well.

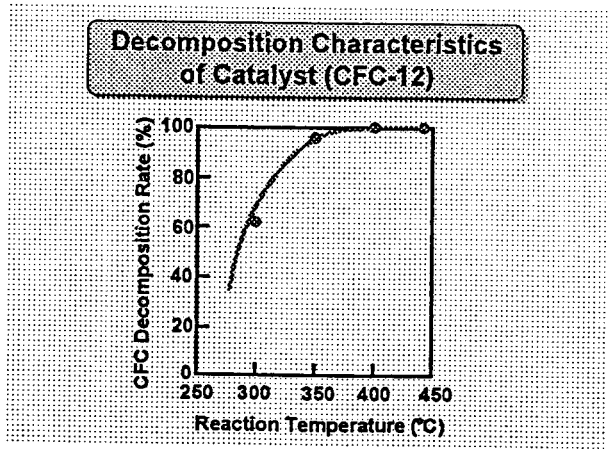

Figure 5

4.3 Schematic Diagram

A schematic diagram of the system is illustrated in figure 6. The system consists of a preheating unit, a reaction chamber, a cooling and absorption vessel, an alkaline chamber, a sedimentation unit, a de-watering unit and a water reservoir.

Preheated air and water are mixed with CFCs and introduced into the reaction chamber containing the newly developed catalyst.

Decomposed chemicals react with the calcium hydro-oxide in the cooling and absorption vessel.

Calcium fluoride and calcium chloride are separated from the calcium hydro-oxide solution at the sedimentation and de-watering unit.

Calcium hydro-oxide stored in the treated water reservoir is returned to the alkaline chamber and reused.

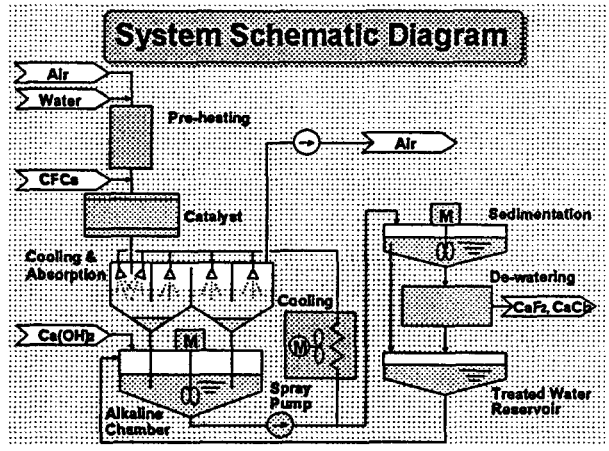

Figure 6

4.4 Catalyst and Sludge

The picture of catalyst is shown in the left side of Figure 7. Decomposed Fluorine and chlorine from CFCs react with calcium hydro-oxide and are finally de-watered. The right picture in Figure 7 illustrates the sludge.
It can be used for raw materials in the chemical industry.

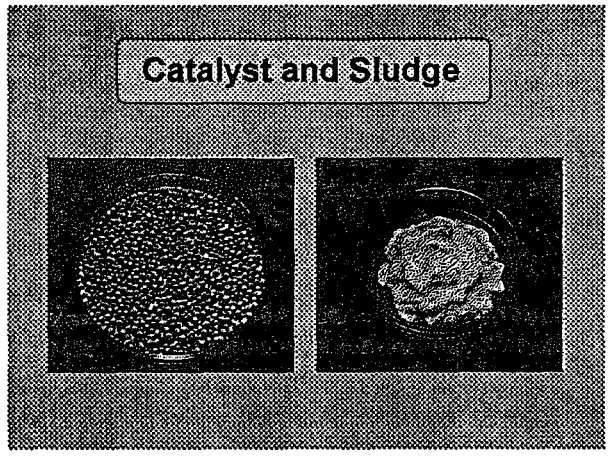

Figure 7

4.5 System Appearance and Specification

The entire system is illustrated in figure 8 and the specifications of the system are shown in Table 3.

The size of the system is so compact that it is transportable by truck.
The consumption of energy is small since CFCs are decomposed at 400 degree celsius.

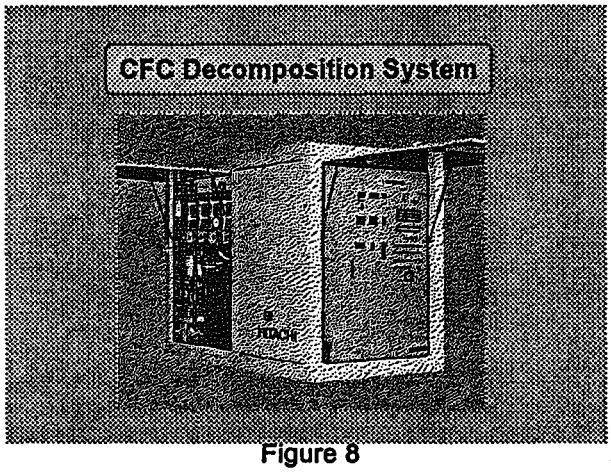

Figure 8

CFC Decomposition System Specifications

Capacity:	1kg/hour(6 hours/day)
Dimensions:	1,600mm(W) 3,000mm(L) 2,200mm(H)
Operation:	Automatic
Utilities:	aprox. 2kw(Electricity) aprox. 30litter/day(Water) aprox. 8kg/day(Slaked Lime)
Others:	Sludge(CaF2 and CaCl2) is recyclable for resources.

HITACHI is ready to supply the unit of which capacity is up to 50kg/hour.

Table 3

Environmentally safe disposal of ozone-depleting CFCs

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1. Introduction

Since their discovery in the thirties chlorofluorocarbons (CFCs) have been widely used, mainly as refrigerants, blowing agents, solvents or cleaning agents because of their outstanding physical and chemical properties such as nontoxicity, nonflammability, their good thermodynamic properties and their low prices. Due to their chemical inertness they are transported to the stratosphere where they are decomposed by UV radiation, and form the reactive catalytic substances that deplete ozon. Chlorine atoms dissociated from CFCs in an altitude of about 18 km are believed to be responsible for diminishing the ozone content of the stratosphere. This would lead to an increase in harmful UV-B radiation reaching the earth's surface.

As a result of these findings the "United Nations Environmental Protection (UNEP) Protocol on Substances that Deplete the Ozone Layer" was adopted in September 1987. An agreement was reached first on a freeze followed by a scaled reduction in the production of CFCs. Owing to the "Montreal Protocol" the production and use of CFCs will be prohibited (as of 1/1/1995 in the European Union and as of 1/1/2030 worldwide).

2. Technological Background

In the middle of the eighties the annual gross production of CFCs was increased to a scale of several million tons. 1986 approximately 10^6 tons of CFCs were produced worldwide. The estimated emissions into the atmosphere were nearly 80 % of this amount. The main application fields of CFCs are shown in Fig. 1. The use of CFCs as refrigerants in equipment with semi-hermetic or open compressors give the main contribution to emission of CFCs. Almost two-thirds of the refrigerant amounts are used for recharging, i.e., to replace refrigerant that has been released.

In order to prevent the further emission of CFCs, the ozone depleting refrigerants still in use have to be recovered, hence methods of collection, disposal and destruction of refrigerants will

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become important. The recovered waste refrigerants have to be replaced by suitable compounds having no ozone depletion potential but affording almost the same thermodynamic properties.

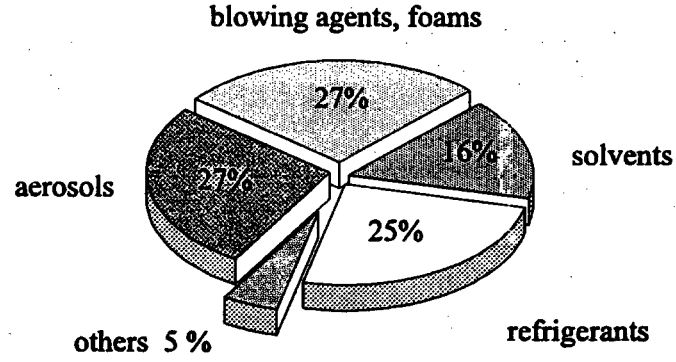


Fig. 1: Applications of CFCs worldwide

In order to speed up the phaseout of the use of CFCs as refrigerants, the midterm transition compounds will be based on HCFCs having only a limited effect on the ozone layer. These so called "Retrofit"blends for the conversion of CFC-12 and CFC-502 plants contain HCFC-22 ($CHClF_2$) as the main substance and can therefore be used with previous equipment and lubricants. However, due to the inclusion of chlorine, they must be viewed as transitional service chemicals only and not as long term solutions for new equipment. The final goal is the use of non ozone-depleting refrigerants based on such compounds as CH_2F_2 (HFC-32), CH_2F-CF_3 (HFC-134a), or CHF_2-CF_3 (HFC-125). Especially HFC-32 or mixtures thereof are thought to be one of the most promising candidates for replacing HCFC-22, which has been mainly used as a low-temperature refrigerant in heavy duty cooling applications. HFC-32 exhibits excellent cooling properties and, in addition, a lower global warming potential than HFC-134a.

Thus the branch of refrigerants faces the task of the environmentally safe disposal of waste refrigerants based on CFCs and the problem of the development and production of currently expensive alternative replacements.

Conventional technologies for the disposal of CFCs are mainly based on non-catalytic decomposition processes like pyrolysis or incineration, and on catalytic decomposition technologies such as catalytic oxidation, hydrolysis and hydrogenation. However, it would be particularly desirable if recovered CFCs were not only decomposed, but converted to harmless and preferably to useful chemicals in a common process. Seeing as there is not enough destruction capacity for the recovered waste CFCs and also that the market for CFC-replacements such as HFC-32 is growing, it is a challenging and profitable task is to convert the waste CFCs into valuable HFCs.

3. Hydrodechlorination of CFCs to HFCs

In contrast to the conventional technologies the selective hydrodechlorination of CFCs provides an alternative CFC disposal to chlorine free hydrogenated fluorocarbons (HFCs). In 1986 the chlorine containing compounds CCl_2F_2 (CFC-12: 42 %), $CHClF_2$ (HCFC-22: 48.5 %) and CF_3-CF_2Cl (CFC-115: 6.2 %) represented almost 96.7 % of the overall consumption of refrigerants in Germany. Now after the coming into force of national regulations these CFC wastes have to be disposed of. They are recovered as pure compounds or as mixtures thereof. By the use of suited catalysts all these waste compounds can be converted into useful HFCs as described in equations 1 - 3:

$$\underset{\text{CFC-12}}{CF_2Cl_2} + 2\,H_2 \xrightarrow{\text{catalyst}} \underset{\text{HFC-32}}{CF_2H_2} + 2\,HCl \qquad \text{(eq. 1)}$$

$$\underset{\text{HCFC-22}}{CHF_2Cl} + H_2 \xrightarrow{\text{catalyst}} \underset{\text{HFC-32}}{CF_2H_2} + HCl \qquad \text{(eq. 2)}$$

$$\underset{\text{CFC-115}}{CF_3CF_2Cl} + H_2 \xrightarrow{\text{catalyst}} \underset{\text{HFC-125}}{CF_3CF_2H} + HCl \qquad \text{(eq. 3)}$$

The resulting HFCs do not have any ozone depletion potential due to the absence of chlorine. Thus, they can be used as alternative refrigerants in industry. The intended process of the selective hydrodechlorination of CFCs should have the following advantages:

- CFCs are disposed of in an environmentally safe way,
- CFCs are used as valuable raw material,
- the produced HFCs can be sold as components of commercial refrigerants (HFC-410 etc.)

The conversion of waste CCl_2F_2 (CFC-12) into the high added value product CH_2F_2 (HFC-32) seems technically and economically feasible with selected metal modified palladium on activated carbon catalysts, which are subjects of several patents. Tables 1 ans 2 show the effect of the substrate on the product distributions.

table 1: Product distribution for the hydrodechlorination of CFC-12 and HCFC-22 at a reaction temperature of 200°C and 250°C respectively

substrate	selectivities [%]			
	alkanes	CH_2F_2 (HFC-32)	CH_3F (HFC-41)	$CHClF_2$ (HCFC-22)
CCl_2F_2 (CFC-12)	19.5	79.1	0.6	0.8
$CHClF_2$ (HCFC-22)	11	87.6	1.4	-

table 2: Product distribution for the hydrodechlorination of CFC-115 at 250°C

substrate	selectivities [%]	
	CF_3-CHF_2 (HFC-125)	CF_3-CH_2F + CF_3-CH_3 + CHF_2-CHF_2 (HFC-134a + HFC-143a + HFC-134)
CF_3-$CClF_2$ (CFC-115)	99.6	< 0.4

The conversion of the substrate was in all cases higher than 98 %. Remaining unreacted CFCs and undesired chlorine containing intermediate compounds were subsequently removed by catalytic purification. When carrying out such a process on a commercial scale one could take profit from the following technological advantages:

- The process is exothermic.
- Depending on the catalysts used one can even dispose of blends of refrigerants as obtained from industry and convert them into high purity products.
- The process works with high selectivity. This makes it attractive even for small enterprises which neither own capacities for CFC-disposal nor for their own production of HFCs.
- The process of hydrodechlorination of CFCs needs only hydrogen and the catalyst, but provides HFCs and industrial acids (HCl/HF) of commercial quality

Such a coupling of waste disposal with the production of alternative refrigerants makes the whole process highly flexible and cost effective, and should therefore be of special interest for enterprises in the refrigeration field which have to dispose of CFCs and own no capacities for HFC-production.

4. Preferred applications of a hydrodechlorination process

4.1. Disposal of CFCs from waste refrigerants

In a pilot plant we will convert the widely used and large scale recovered CFCs freon-12 and freon-502, which is a mixture of 48.8 % HCFC-22 and 51.2 % CFC-115. Due the difference between the reactivities of CFC-12 and CFC-115/HCFC-22, freon-12 and freon-502 have to be treated under different reaction conditions (cycles A,B). The concersion of CFC-12 gives 99 % HFC-32. HFC-32 itsself represents a commercial product (freon-32) that is used as low-temperature refrigerant in heavy duty cooling applications. The conversion of freon-502 gives a mixture consisting of HFC-125 and HFC-32. In this case marketable freons-410A,B can be obtained by adding controlled amounts of HFC-32 from cycle (A) to the products of cycle (B). Our concept of process design further involves the possibility to introduce commercial available freon-134a. This expands the variety of products by the freons-407A,C.

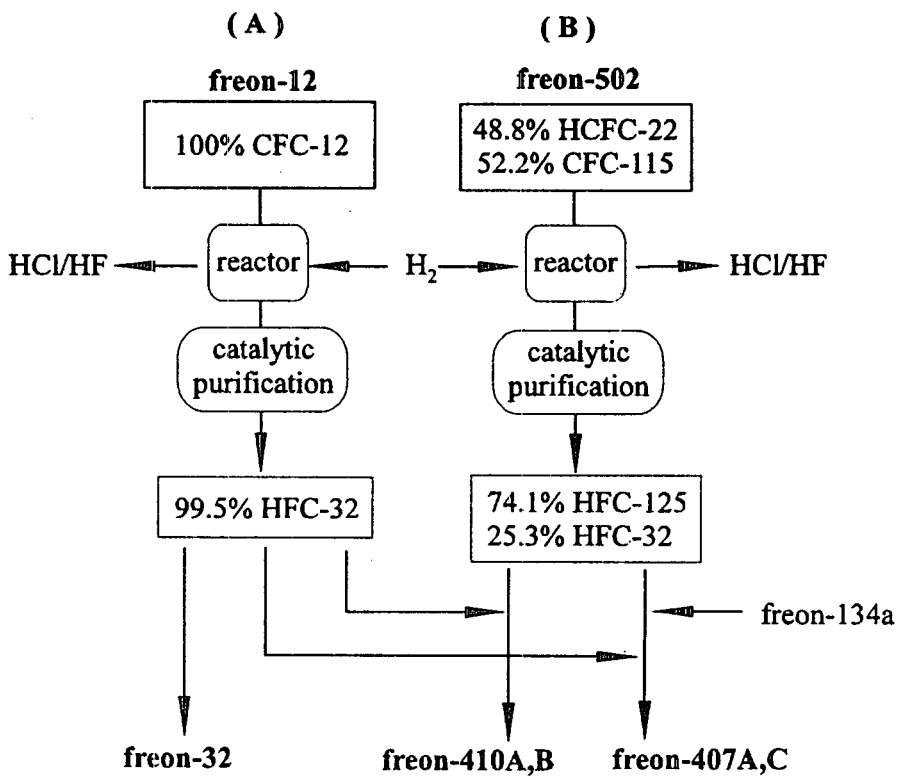
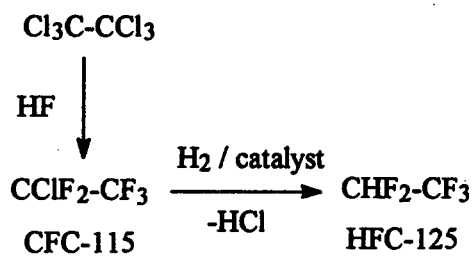


Fig. 2: conversion of waste refrigerants into chlorinr free replacements

4.2 Conversion of CFC-115 production lines to manufacture of HFC-125

CFC-115 (ClF_2-CF_3) is manufactured on an industrial scale by the fluorination of hexafluoroethane with hydrogenflouride (HF). These plants could easily be transformed to produce HFC-125 (CHF_2-CF_3) by attaching an additional hydrodechlorination step, i.e. converting the primary product CFC-115 into HFC-125. Thus, the existing production plants for CFC-115 could be used for the manufacture of ozone safe refrigerants.



This would decrease the investments necessary for the setup of new production lines which are important for the speed up of the phaseout of production and use of CFCs, especially in the countries of eastern Europe and Asia. According to international agreements, today's annual production of about several thousand tons of CFC-115 in that countries should be reduced to zero by the year 2030.

4.3. Purification of conventionally produced HFCs

Generally HFCs are produced from the respective chlorinated hydrocarbons by fluorination treatments using selected catalysts in the liquid or vapour phase. Due to that method of production the product gas stream always contains traces of chlorine containing intermediate products. A catalytically purification treatment could simplify or even avoid the expensive distillative separation of this contamination.

The above mentioned undesired chlorine containing contamination can be reduced to several ppm without significant loss of the valuable HFC. Such purity is important for special applications like propellants for medical sprays. Today CFC-12 is still used for these applications. Its substitution for HFC-32 is a challenging task. Medical applications will create a growing market in the next years.

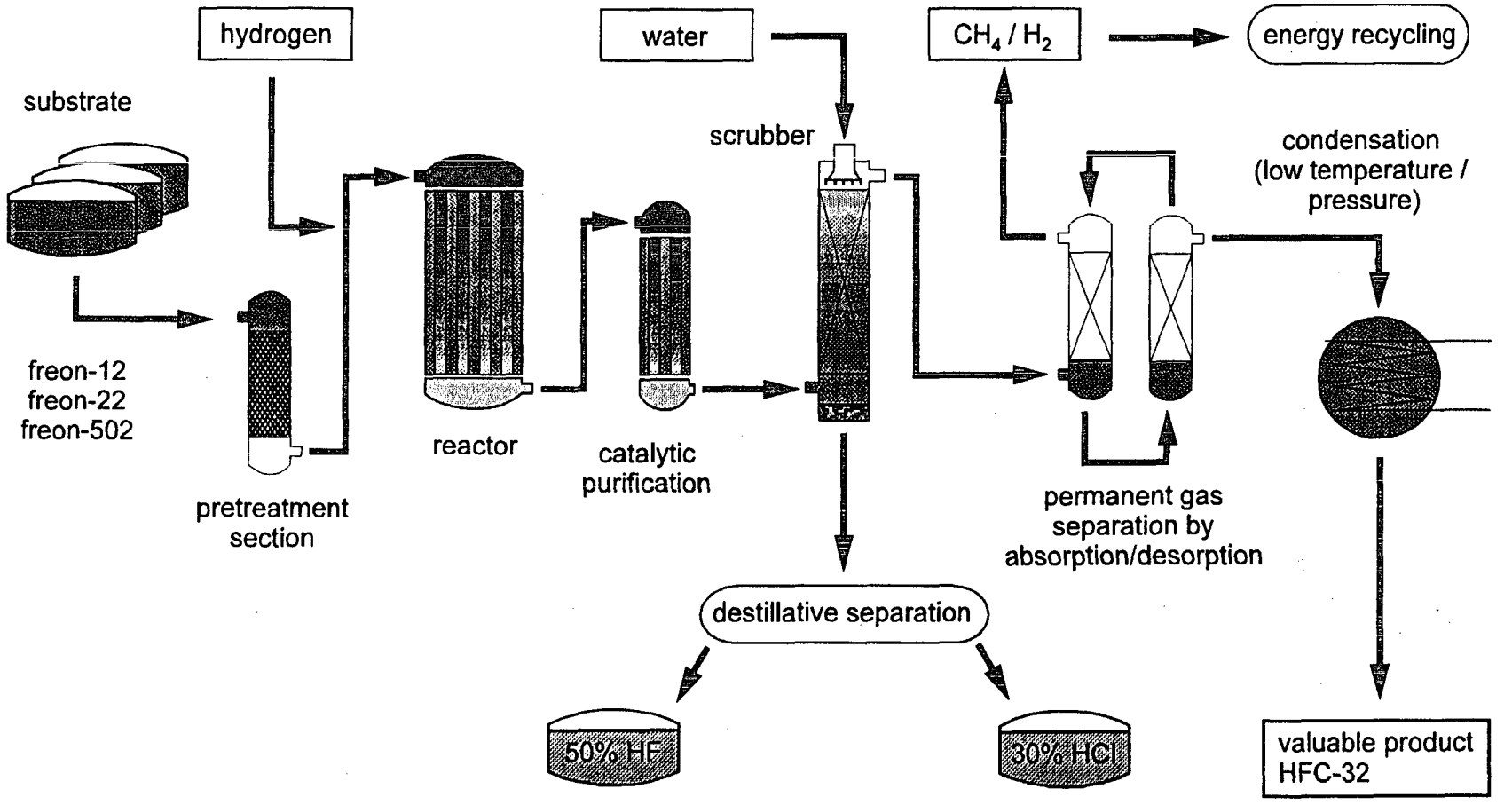


Fig. 3: Block sheme for the process design for the hydrodechlorination of CFC-12 (CCl_2F_2)

5. Process design

A process design for the selective hydrodechlorination of CFCs has been made based on a capacity of 1 kg/h. Important design considerations are the exothermicity of the reaction and the need for the removal of HCl/HF and H_2/CH_4 from the products. The technical feasibility of the complete process design was proved on a laboratory scale. No unsurmountable barriers were encountered. A scheme of the designed process is depicted in Fig. 3.

The feed of the plant consists of recovered waste CFC-12, waste HCFC-22 or CFC-115. These raw materials contain contaminants such as oil or water which must be removed by a pretreatment before the feed enters the reactor. Because of the highly exothermic reaction a multi-tube liquid cooled fixed bed reactor has been chosen. The heat transfer fluid allows reaction temperatures in the range of from 150°C up to 300°C, depending on the substrate being fed.

Because of the large difference in the reactivity between CFC-12 and HCFC-22, a recycling of the intermediate product HCFC-22 is not useful and a one time operation with 100% CFC conversion is preferred. In order to reach complete conversions, an additional catalytic purification step is used. Using a special hydrodehalogenation catalyst, the intermediate products HCFC-22 and HFC-41 (CH_3F) are converted to methane. The loss of the target compound HFC-32 during this purification step is less then 1 %. Thus the product gas stream contains only HCl/HF, alkanes and excess hydrogen in addition to the target product.

Therefore the further product purification is divided into two steps. First the acids (HCl and HF) are removed from the gas stream and subsequently the permanent gases methane and hydrogen are separated from the target HFCs. The HCl and HF are scrubbed with water to yield a mixture of aqueous hydrochloric and hydrofluoric acid. A destilative separation yield the pure acids. This is state of the art. The permanent gases are separated by an absorption/desorption step. The desorbed fluorocarbons are pressurized and condensed. The liquefied component is then pumped away and filled to gas cylinders.

6. Conclusions

Waste refrigerants recovered from industry, such as freon-12, freon-115, freon-502 and freon-22, can be easily converted into the valuable chlorine free products, which may be recycled into the market.

A high selectivity to HFC-32 can be combined with a complete CFC-12 conversion by using an additional catalytic purification step. Thus the conventional extensive purification by pressure distillation or low-temperature distillation can be avoided. The content of the toxic HCFC-31 in

the target HFC-32 is below 10 ppm, which also makes the HFC-32 attractive for medical applications.

A pilot plant with a capacity of about 1 kg/h was designed and will be tested for the conversion of waste freon-12 into HFC-32 within this year.

The preliminary process design has shown that the conversion of CFC-12 into the high added value product HFC-32 is both technically and economically feasible. The design can easily be extended to a process for conversion of both HCFC-22 and CFC-115 into HFC-32 and HFC-125 respectively.

A process based on the investigated catalyst systems could be an important tool in the protection of the ozone layer. The selective hydrodechlorination using heterogeneous catalysts thus represents a technologically promising and economically valuable contribution to solving the global problem of ozone depletion.

Acknowledgements

I would like to express my gratitude to the Ministry of Economy of the Federal Republic of Germany and the Ministry of Environmental Affairs of the Land Brandenburg for their financial support.

New Cyclic HFC

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1. Introduction

1,1,2,2,3,3,4-Heptafluorocyclopentane (HFCPA, figure 1) is a new cyclic HFC which has better properties than 1,1,2,2,3,3,4,5-Octafluorocyclopentane (OFCPA, figure 2).

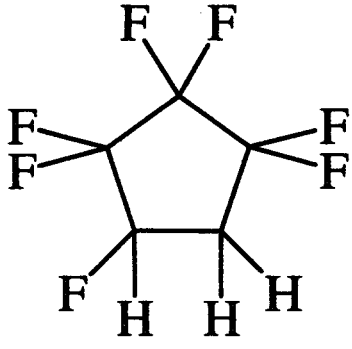


Figure 1 "HFCPA"

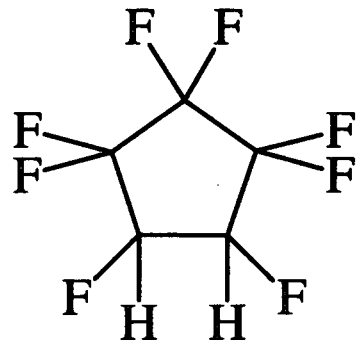


Figure 2 "OFCPA"

Last year we reported about OFCPA that has useful properties: nonflammability, reasonable boiling point, miscibility with hydrocarbons under high temperature, short atmospheric life-time, and zero ozone depletion potential. Besides OFCPA, we have investigated a new

chemical with better chemical stability and shorter atmospheric lifetime than OFCPA, consequently we have succeeded to develop HFCPA.

Another important finding is that Octafluorocyclopentene (OFCPE, figure 3) is useful for the dry etching process[1)] in the semiconductor industry.

In this paper, we report about these two new chemicals.

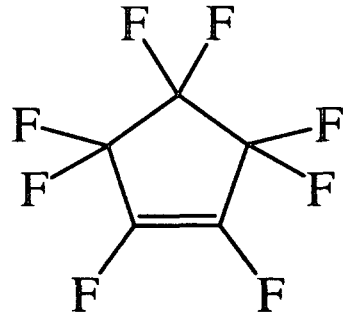


Figure 3 "OFCPE"

2. Structural Features

As shown in figure 1, HFCPA is a cyclic HFC and has a distinctive moiety, i.e., "-CFH-CH_2-". It is important that at least one of the neighboring groups of "-CFH-" is methylene (i.e., -CH_2-) group. This characteristic structure contributes to the chemical stability of HFCPA.

Table 1 (Relative Stability under Alkaline Conditions)

Name	HFCPA	HFC-43-10	OFCPA
Chemical Structure	$CF_2CF_2CF_2$ / $CFHCH_2$	$CF_3CFHCFHCF_2CF_3$	$CF_2CF_2CF_2$ / CFHCFH
Relative Stability*	>		≥
Flammability	non-flammable	non-flammable	non-flammable

*Each substrate was treated with 8N-K_2CO_3aq for an hour at 30℃.

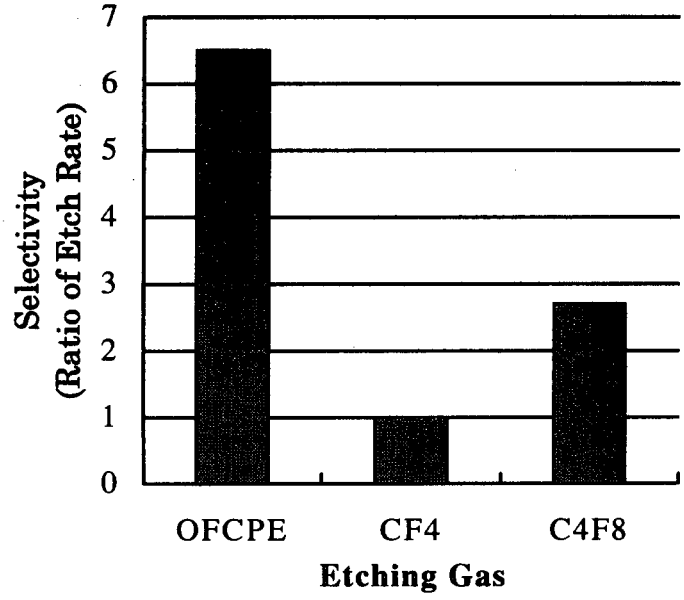
Table 1 shows relative chemical stability of some fluorine compounds under alkaline conditions. -CFH-CH_2- is more stable than -CFH-CFH-.

1,1,2,2,3,3-hexafluorocyclopentane, which has -CH_2-CH_2- moiety, is even better at stability than HFCPA; however, we selected to use HFCPA, which has -CH_2-CFH- moiety, because:

(i) HFCPA is nonflammable and stable enough. (ii) 1,1,2,2,3,3-hexafluorocyclopentane is flammable.

OFCPE has a double-bond in its molecule which leads to a shorter atmospheric lifetime than that of corresponding cycloalkane OFCPA, although OFCPE is classified as a perfluorocarbon (PFC). Figure 4 shows OFCPE is superior for plasma dry-etching to conventional gases that are saturated PFC having long atmospheric lifetime. The high selectivity is an important factor for plasma dry-etching.

Figure 4
OFCPE Application to Plasma Dry Etching
"Ratio of Etch Rate (SiO_2 vs Poly-Si)"
conditions: Plasma Density = $10^{11}/cm^3$
60sec.



3. Physical Properties

Table 2 shows some physical properties of HFCPA. The boiling point of this material is reasonably high, so that it is easy to treat and recover the solvent in the actual application process.

Table 2 (Physical Properties at 25℃)

	OFCPE	HFCPA	OFCPA	C_6F_{14}	HFC-43-10	CFC-113
Formula	C_5F_8	$C_5F_7H_3$	$C_5F_8H_2$	C_6F_{14}	$C_5F_{10}H_2$	$C_2Cl_3F_3$
Chemical Structure	Figure3	Figure 1	Figure 2	$CF_3(CF_2)_4CF_3$	Table 1	$CFCl_2CF_2Cl$
Molecular Weight	212	196	214	338	252	187
Boiling Point (℃)	27	82	79	56	55	48
Flammability	none	none	none	none	none	none
Density (kg/m^3)	1580	1580	1680	1680	1580	1560
Viscosity (mPa·s)		1.1*	1.7	0.4	0.67	0.68
Surface Tension (mN/m)		18.0*				
Sol. in aq. (ppmw)	75.6	720	6820		140	170

*measured at 45℃

4. Environmental Effect and Toxicity

Table 3 shows that atmospheric lifetime of OFCPE, 1.1years, is the shortest and the calculated lifetime of HFCPA, 1.7years, calculated by Cooper's method, is also short. Ring strain may contribute to the fact that atmospheric lifetime of these cyclic fluorine compounds is shorter than that of these linear compounds such as HFC-43-10. Atmospheric lifetime value is being measured based on the reaction rate of HFCPA with the OH radical.

Table 3 (Environmental Properties)

		OFCPE	HFCPA	OFCPA	C6F14	HFC-43-10	CFC-113
Atmospheric Lifetime (Years)	calcd.	0.12	1.7	4.7			
	found	1.1		3.7	3200	17	85
ODP (CFC-11=1)		0	0	0	0	0	0.8

HFCPA has no acute toxicity (Table 4), and other tests are under way.

Table 4 (Toxicity of HFCPA)

Acute Toxicity	
Rat Acute Oral Toxicity Study	LD50 > 2000 mg/kg
Rabbit Skin Irritation Study	Not irritant
Ames Test	Negative
Rabbit eye irritation study	Not irritant
Guinea-pig skin sensitization study	Not irritant
Rat acute inhalation toxicity study LC 50 (4hours)	practically no toxic 15000ppm
Advanced Toxicity	
Readily Biodegradation Study	Not Readily Degradable
Rat 90days Inhalation Toxicity Study	to be obtained
Rat Teratology Study by Inhalation	to be obtained
Dog Cardiac Sensitization Study	to be obtained

5. Application to Precision Cleaning

As shown in Table 5, almost all the plastics and elastomers can be used with HFCPA.

Table 5 (Chemical Attack to Plastics and Elastomers)

Plastics	rate of weight change (%)*		Plastics	rate of weight change (%)*	
PVC, soft	-0.005	A	PFA	0.055	A
PVC, hard	0.72	A	PPS	0.0	A
PP	0.07	A	Cycloolefin-Polymer: ZEONEX™	0.034	A
PS	0.003	A			
PC	-0.08	A	**Elastomers**		
PE	0.05	A	SBR	-0.98	A
Polyacetal	-0.003	A	Silicone Rubber	10.80	D
Bake-Phenol	-0.09	A	NBR	21.38	D
Polyurethane	34.19	D	BR	-0.80	A
66-Nylon	-0.08	A	Polychloroprene	-0.32	A
Acrylic	-20.63	D	Fluoro Elastomer: Karletz™	2.02	B
ABS	0.08	A			
Epoxy resin	-0.013	A	Fluoro Elastomer: Viton™	111.68	D
PTFE	0.099	A			

*4hours immersion at 50℃, weight-%; A:<1%, B:1-3%, C:3-5%, D:>10%

HFCPA is suitable for a co-solvent cleaning system, because higher hydrocarbons are not dissolved in HFCPA under low temperature; however, they are dissolved easily under high temperature. Higher hydrocarbons are well-known as good solvents for oils, waxes, and various greasy or oily soils. In addition, HFCPA in combination with various other solvents can be used for a single-solvent cleaning system, since almost all polar solvents and lower hydrocarbons are dissolved in HFCPA (table 6).

Table 6 (Solubility)

Solvent \ Temperature (℃)	5wt%-Solubility*			Solvent \ Temperature (℃)	5wt%-Solubility*		
	10	20	80		10	20	80
n-heptane	○	○	○	1-butanol	×	○	○
2,2,4-trimethylpentane	○	○	○	2-butanol	○	○	○
n-decane	×	×	○	cyclopentanol	×	○	○
n-tridecane	×	×	○	n-butyl ether	○	○	○
toluene	○	○	○	2-pentanone	○	○	○
1-bromopropane	○	○	○	cyclopentanone	○	○	○
ethanol	○	○	○	2-heptanone	○	○	○
IPA (2-methylethanol)	○	○	○	water	×	×	×

*○: clear homogeneous solution, 5wt% of the solvent was dissolved in HFCPA

×: heterogeneous solution, 5wt% of the solvent was mixed with HFCPA

6. Application to Specialty Solvents

To make lubricant layer on the surface of hard-disks, fluoroether-polymer dissolved in PFC has been used conventionally. Recently, it was found that HFCPA is applicable as an alternative to the PFC solvents that have long atmospheric lifetime. Table 7 shows coefficients of friction, which is an important property for lubricant layer .

Table 7 (Application to a solvent for lubricant*)

	HFCPA	conventional solvent (PFC)
Coefficients of Friction	0.40	0.52

*A 0.2wt% of lubricant (fluoroether-polymer) was dissolved in each solvent.

7. Summary

HFCPA is a new cyclic HFC and shows the following unique characteristics:

1. Short atmospheric lifetime (1.7years, calculated)
2. Zero ozone depletion potential
3. Reasonably high boiling point (82℃)
4. High solubility in/of hydrocarbons
5. Various applications:
   i. Co-solvent cleaning system
   ii. Single solvent cleaning system
   iii. Solvent for fluorinated materials

The characteristics of OFCPE are:

1. Cyclic and olefinic PFC
2. Very short atmospheric lifetime (1.1years)
3. Zero ozone depletion potential
4. Low boiling point (27℃)
5. Applications:
   i. Plasma dry-etching gas.
   ii. Starting material for HFCPA synthesis

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[1] Shunji Sasabe, *SEMI Technology Symposium 96 Proceedings*, S-19, Nov. 1, 1996, Semiconductor Equipment and Materials International

normal-Propyl Bromide Based Cleaning Solvents

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Abstract

Since their introduction last year, new solvent systems based on *normal*-propyl bromide (nPB) have been successfully utilized in many different applications. These materials were developed as cost-effective replacements for chlorinated alkanes and alkenes. The new systems have similar physical and cleaning properties to 1,1,1 trichloroethane (TCA). *n*-Propyl bromide based systems have low Ozone Depletion Potential (ODP) and no flash point. Included in this talk will be an introduction to a new electronics grade of *n*-propyl bromide based solvent. Data will be presented showing the efficacy of this material for cleaning electronic parts. Also, user case histories will be presented demonstrating the utility of *n*-propyl bromide cleaners in a wide variety of applications.

Introduction

The introduction of chlorinated solvents provided manufacturers and fabricators a convenient and economical way to clean a host of difficult soils from strategic parts. Efficient cleaning, rapid drying, low flammability, residue free parts and relatively low solvent costs all contributed to the popularity of chlorocarbon fluids. However, many chlorine containing solvents have now been banned or restricted because of environmental and/or health considerations. In the search to find suitable alternatives, a wide variety of new solvents were developed[1]. Many of the new solvent cleaners do excellent jobs, but still suffer from one or more deficiencies relative to the overall cost/performance of the chlorinated materials they replaced. Even some of the newer solvents, such as some hydrochloroflouorocarbons (HCFCs), have been shown to have environmental problems and have been banned from usage in cleaning applications.

Background

In 1991, the total U.S. market for 1,1,1-trichloroethane (TCA) as a cleaning solvent was 700 MM lbs. Another 200 MM lbs was sold as an emissive solvent. TCA was very effective and very popular as a cleaning solvent, but it suffers from two important drawbacks relative to environmental considerations. It has a relatively high Ozone Depletion Potential and a relatively high Global Warming Potential. The manufacture of TCA was banned by the Montreal Protocol effective January 1, 1996.

Identification of an across the board replacement for TCA has proved to be a formidable task, and a fragmentation of the cleaning market has resulted.[1] Different products and procedures have been developed for different applications, but not all of these have proven to be wholly satisfactory. As an example, the hydrochlorofluorocarbon HCFC-141b was introduced and seemed satisfactory for a number of niche applications, but it was banned from use as a cleaning agent effective January 1, 1997. It may still be used as a refrigerant.

normal-Propyl Bromide -- An Attractive Alternative

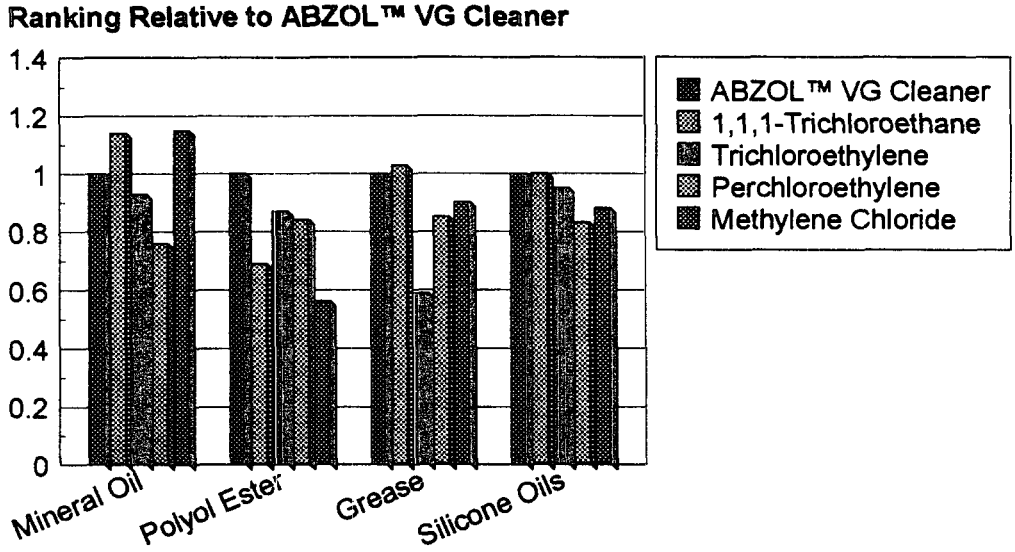
A new solvent/cleaner based on *normal*-propyl bromide (nPB) has been developed to meet the needs of those who require the cleaning efficiency of the chlorinated solvents, but who must meet the strict environmental standards for a replacement solvent.[2] The new solvent/cleaner does not suffer from many of the short-comings of other alternative solvents that have been offered to the market. nPB is an effective cleaning agent. It is safe to use under the proper conditions, has a low ODP and a low GWP, and it is not regulated under most environmental and worker safety rules. It is compatible with metals, has a low tendency to cause corrosion and may be used in most current vapor degreasing equipment. It is easily recycled and is moderately priced.

Cleaning Power

Indicators that relate to the cleaning ability of a solvent are the solubility parameters. These are the Hildebrand Parameter, the Kauri Butanol Number and the Hansen Parameters. The values for nPB for these parameters compare quite well to the common chlorocarbons.

Although solubility parameters provide a guide to cleaning power, they do not take the place of experimental results. In order to compare the cold cleaning ability of nPB to chlorinated solvents, a simple test procedure was devised. Solutions of typical soil contaminants (30 wt%) were prepared in solvent. Steel wool wedges were weighed and then soaked in the contaminated solvent, drained and dried at 100°C for 30 minutes. The wedges were re-weighed and the weight of retained soil recorded. The impregnated wedges were then placed in short glass tubes and washed with 3 ml of the test solvent. The wedges were drained, dried and weighed as before. The grams of soil lost per ml test solvent gives a measure of cleaning power. In Graph 1, the cleaning power is shown relative to the cleaning power of TCA.

Graph 1 shows that nPB based cleaners have fractionally lower cleaning ability than TCA when used to clean mineral oil, equivalent performance on grease and silicone oil, and superior performance in removing polyol esters. This experimental results are consistent with the Hansen Parameters which show that nPB has a slightly lower value for non-polar materials and higher values for polar and hydrogen bonding compounds. Thus, the cleaning power of nPB based cleaners is clearly equivalent to the popular chlorinated solvents that have been banned or restricted.



Cleaning of Electronics Components

The electronics industry faces some cleaning challenges not found in other types of cleaning applications. In particular, it is of utmost importance that ionic residues remaining on integrated circuit boards after soldering operations be removed to very low levels. Cleaners based on nPB and formulated for vapor degreasing have proven to be surprisingly good at the removal of ionics. However, a new formulation designed specifically for the electronics industry has recently been introduced. ABZOL™ EG Cleaner is a narrow boiling range (azeotropic or near azeotropic) blend of nPB, a specifically selected alcohol, and the appropriate levels of stabilizers.

Two independent experiments have demonstrated the high efficiency of the ABZOL™ EG Cleaner formulation for the removal of ionic residues from circuit boards. In one experiment, circuit boards were prepared by a potential customer. They were cleaned and evaluated for cleanliness at Detrex Corporation using an Omega Meter. In the second, circuit boards were prepared by Contamination Studies Laboratories (CSL). These boards were cleaned at the Albemarle Technical Center and returned to CSL for evaluation by the Omega Meter and by Ion Chromatography.

The circuit boards prepared by the potential customer were made of polyimide and were 6"x7" with solder mask on both sides. Each board contained twelve 20-pin LCCs (Leadless Chip Carriers) and two 68-pin LCCs. The LCCs had 50 mil pitch centers (distance between leads). The boards prepared by CSL were IPC-B-36 boards. First they were pre-cleaned to less than 0.1 microgram/sq.in. of NaCl residues. Alpha Metals RA321 RA solder paste was hand applied to the test pads. The paste was reflowed in an oven in the usual fashion. After cooling, the boards

were sprayed with Kester 1585-Mil RA flux and again reflowed.

The cleaning process at Detrex emulated an in-line process at the customer which included immersion in the boiling solvent for 100 seconds and the use of spray wands. The cleaning process at Albemarle employed a batch vapor degreaser with three minutes immersion in the boil sump. Three circuit boards were cleaned by each combination of cleaning process and evaluation. The levels of ionic contamination found on the boards were:

Board No.	Detrex Omega Meter	CSL Omega Meter	CSL Ion Chromatography
1	4.4 μgms/in^2	2.30 μgms/in^2	2.87 μgms/in^2
2	3.9	3.10	2.18
3	6.4	2.70	2.55
Ave.	4.9 μgms/in^2	2.70 μgms/in^2	2.55 μgms/in^2

Standard Requirements

Mil-C-28809	<14.0 μgms/in^2
Mil-STD-2000	<14.0
NASA NHB 5300.4 (3A-7)	<10.0

Contamination Studies Laboratory noted in their report that the maximum historically acceptable level for ionic contaminants is 14.0 μgms/in^2 (see Mil specs above). The report judges ABZOL™ EG Cleaner to perform better than the Freon TMS benchmark.

Environmental and Health Regulatory Status

Worker safety, public safety and environmental protection are paramount in the development of any new product. The current status of n-propyl bromide and solvent/cleaner systems based upon it is:

1. **SARA** - Superfund Amendments and Re-authorizaton Act. This act requires reporting of inventories and emissions of listed chemicals and groups. nPB is not regulated.

2. **HAP** - Hazardous Air Pollutant. A listing of chemicals that the EPA has declared hazardous. nPB is not on the list.

3. **NESHAP** - National Emission Standard for HAP. Sets standards for use of HAPs. Since nPB is not a HAP, these standards do not apply.

4. **RCRA** - Resource Conservation Recovery Act. Defines hazardous wastes and how to manage them. nPB is not regulated under this act.

5. **GWP and HGWP** - Global Warming Potential, Atmospheric Lifetime and Ozone Depletion Potential calculations were carried out in a cooperative effort by Atmospheric and Environmental

Research, Inc. and the Center for Chemical and Environmental Physics at Aerodyne Research, Inc.[3] GWP is calculated relative to CO_2, while HGWP (Halocarbon GWP) is calculated relative to CFC-11. GWP calculations were done using different integration time horizons. By the HGWP method, CFC-11 is ten thousand times more detrimental as a global warming agent than is nPB. By the GWP method, it is fourteen thousand times worse than nPB, and nPB is only one tenth as bad as CO_2.

Compound	HGWP	GWP (20 yrs.)	GWP (100 yrs)	GWP (500 yrs)
CFC-11	1.0	4500	3400	1400
nPB	0.0001	1.01	0.31	0.1

6. **Atmospheric Lifetime** - Ozone Depletion Potentials (as well as GWP) depend on the atmospheric lifetime of the substance in question. Ozone depletion takes place in the stratosphere. In order for a substance to have a high ODP, it must be able to work its way to the stratosphere. The atmospheric lifetime of nPB is only eleven days by the latest estimate.[4] In comparison, TCA has a lifetime of 5.4 years.

7. **ODP** - Ozone Depletion Potential. Models for calculating ODPs have generally been based on the assumption that the chemicals are relatively long-lived in the atmosphere. Because of the short atmospheric lifetime of nPB, certain assumptions had to be made relative to the rate of transport of the molecules and the free radicals that are formed when they dissociate. In a recently published paper, two different models were used, resulting in ODPs of 0.0019 and 0.027.[4] More recently, Professor Don Wuebbles and associates at the Department of Atmospheric Sciences, University of Illinois, has determined that the ODP for nPB is only 0.006.[5] For comparison, TCA has an ODP of 0.1.

8. **PEL** - Permissible Exposure Limit. This is the concentration of a material in the air that a worker can be safely exposed to over a time weighted eight hour work day, five days per week. Albemarle has set an Albemarle Workplace Exposure Guideline (AWEG) of 100 ppm based on 90 day inhalation tests.

9. **VOC** - Volatile Organic Compound. All volatile organic compounds are classified as VOCs until there is experimental evidence that they do not contribute to the formation of smog. Therefore, nPB is currently classified as a VOC and must be used in accordance with local regulations regarding VOCs. Studies are currently under way at the Statewide Air Pollution Research Center, University of California, Riverside, to determine the degree of photo reactivity of nPB and the types of photochemical products formed. The EPA will review this data to determine if nPB can be declassified.

10. **SNAP** - Significant New Alternatives Policy. This is the policy under which EPA gives approval for the marketing of a replacement for an ozone depleting chemical. EPA may approve, disapprove or give restricted approval within ninety days of the application. Alternatively, EPA

may choose to delay any ruling on an application. If the EPA does not rule within ninety days, the replacement chemical may be commercialized. ABZOL™ Cleaners are approved for sale pending further review by the EPA.

The H&E regulatory status for ABZOL™ Cleaners is summarized in Table II.

Summary

Solvent/Cleaner systems based on n-propyl bromide have been introduced as replacements for chlorinated solvents in cleaning applications. nPB is an aggressive, fast drying solvent that is suitable for a variety of difficult cleaning and degreasing applications. The use of nPB based solvents is not regulated under SARA, HAP, NESHAP or RCRA, and they are approved for sale under SNAP (further review by EPA possible). nPB has low potentials for ozone depletion and for global warming, but it is currently classified as a VOC. The Albemarle Workplace Exposure Guideline is 100 ppm, which makes it safe to use with the proper precautions for worker safety. In demanding applications like electronics cleaning, nPB based formulations have been demonstrated to be very effective in ionics removal.

TABLE II
Environmental and Health Regulatory Status

Regulation	ABZOL™ Cleaners	1,1,1-Trichloroethane	Trichloroethylene
SARA	No	Yes	Yes
HAP	No	Yes	Yes
NESHAP	No	Yes	Yes
RCRA	No	Yes	Yes
HGWP	0.0001	0.023	Almost Zero?
ODP	0.006[4]	0.1	Almost Zero?
Atmospheric Lifetime	11 days[4]	5.4 years	??
PEL	100 ppm*	350 ppm	50 ppm
VOC	Yes	No	Yes
SNAP	Approved for Sale Pending Review	Unacceptable	Acceptable

* Albemarle Workplace Exposure Guideline

Case Histories

1. Electronic Equipment

A company that produces electronic components for clinical equipment used in biomedical applications had used CFC 113 blends in both liquid and vapor phase defluxing[5]. Exacting performance standards, rate of throughput, space limitations, limited capital equipment budget and lack of an adequate industrial water system were major constraints on a changeover to a new cleaning system.

The company attempted to switch to a system based on d-limonene. Residue from the cleaning agent, buildup of rosin flux and reactivity to produce assorted oxidation products made the electronic components unsuitable for use. An unacceptable green residue remained on the assemblies and there was an increase in product failures.

After switching to a cleaning solvent made from n-propyl bromide (ABZOL™ VG Cleaner), the company found that the new cleaner did a better job of removing flux than the CFC-113 blend. There were no residue problems as there were with d-limonene. Some of the plastic components did show some discoloration, but this problem was solved by shortening the exposure time -- an added benefit by increasing throughput.

2. Implantable Body Parts

Smith & Nephew Orthopedics (Memphis, TN) manufactures artificial body parts, such as hip joints, for implantation. The parts consist of a titanium bone replacement and an Ultra High Molecular Weight Polyethylene (UHMWPE) cartilage replacement. Standards for cleanliness are, of course, very high. In addition, Smith & Nephew expressed concern about retention of solvent in the UHMWPE parts. A final criteria is that the cleaning solvent must kill at least 50% of the bacterial spores on an artificially inoculated UHMWPE part. There were two cleaning solvents that Smith & Nephew wished to replace in their process. The first was based on HCFC-141b. The second was based on trichloroethylene.

The initial set of experiments were for part cleanliness, and these were performed at Baron·Blakeslee, Inc. (Long Beach, CA). UHMWPE parts were exposed to ABZOL™ Cleaner vapors for 90 seconds. Both cleaned and uncleaned parts were returned to Smith & Nephew, who found the cleaning to be satisfactory. Acetabular components and hip stems were contaminated with buffing compound. These were cleaned using the Baron·Blakeslee AutoBatch vapor degreaser. The cycle consisted of 30 seconds in the vapor, 5 minutes immersion in the ultrasonic sump at 130°F, 2 minutes TopHat drying and 2 minutes freeboard dwell. The parts were reported to be completely dry with no solvent drag out. Baron·Blakeslee returned the parts to Smith & Nephew, who determined that the cleaning was satisfactory. In a third experiment, a femoral with finger prints was exposed to vapor for 90 seconds. Evidence of fingerprints remained after this test.

The second Smith & Nephew concern was retention of the solvent by the UHMWPE parts. ABZOL™ VG Cleaner was compared directly with commercial cleaning grades of HCFC-141b and trichloroethylene. The test procedure was to place five parts in the boiling solvent for three (3) minutes. The parts were removed and placed in the same solvent at ambient temperature for two (2) hours. The parts were then removed and placed in an open dish. The dish was left in a fume hood with the fan going until it was time to take the measurements. To obtain the quantity of headspace vapors, the parts were placed in a sealed glass chamber and allowed to equilibrate for one (1) hour. The vapors were then analyzed using Gas Chromatography/Mass Spectrometry and quantified against a standard. Measurements were taken at 24 hrs. and 96 hrs. for the ABZOL™ VG. For the other two solvents, the measurements were at 24 hrs. and 106 hrs. The amount of vapor in the headspace has been converted to ppm by volume.

	Concentration of Solvent in Headspace	
	24 hrs	96 or 106 hrs
ABZOL™ VG	30 ppm	3.7 ppm
HCFC-141b	169 ppm	4.4 ppm
Trichloroethylene	469 ppm	27 ppm

These experiments indicate that the ABZOL™ VG Cleaner is retained in the UHMWPE parts to a lesser extent than either the HCFC-141b or the trichloroethylene.

The third criteria was that the solvent/cleaner reduce bacterial spore counts on the UHMWPE parts by at least 50%. Smith & Nephew supplied two sets of parts (six parts each) contaminated with Spordex® *Bacillus Subtilis (globigii)* spores. Each set was divided into two sets of three parts each -- one set to be cleaned and one set as a control. The cleaning procedure was:

1. Tests parts were placed in the basket of a laboratory vapor degreaser and covered with a metal screen to prevent the parts from floating to the surface. The degreaser contained ABZOL™ VG Cleaner.

2. The basket was lowered into the vapor zone and remained there until condensation stopped.

3. The basket was then lowered into the boil-up sump (71°C) for 3 minutes (Set A) or 1.5 minutes (Set B).

4. The parts were placed in the rinse sump for 1 min. followed by the vapor zone for 1 min. The basket was allowed to hang in the free board zone for an additional minute to assure that the parts were dry.

The two sets of cleaned parts along with the accompanying control sets were returned to

Smith & Nephew for analysis. The bioburden validation was done at Axios, Inc. (Kennesaw, GA). The results were:

Sample	Spore Count	% Reduction
Sample A		
Control	5.5×10^6	
Cleaned	1.5×10^6	73%
Sample B		
Control	8.8×10^6	
Cleaned	2.8×10^6	68%

3. Aluminum Parts for Optical Applications

A manufacturer of optical equipment that uses anodized aluminum components. The parts have lettering and other markings on them. The customer requested an evaluation to make sure that the markings would not be damaged in the normal cleaning process. They sent four sets of components, each set containing six different parts. Two sets were cleaned in ABZOL™ VG Cleaner by immersing in the boil-up sump for ten minutes followed by one minute in the rinse sump. The other two sets were immersed for only three minutes in the boil-up sump and then one minute in the rinse sump. All twenty-four parts were returned to the customer for examination. No damage to the parts was observed.

4. Electric Motor Stators

The Galley Products Division of B/E Aerospace had a need to clean burnt oils from used electrical motor stators. They sent two such stators for cleaning. One was clean and the other was covered in oil. Both were cleaned using ABZOL™ VG Cleaner. They were first lowered into the vapor zone of a vapor degreaser and held there until condensation of the vapor on the parts ceased. This required about 5 minutes. They were then lowered into the ultrasonic bath for ten minutes and back into the vapor zone for 5 minutes. The parts were returned to B/E for examination.

B/E Aerospace reported that the parts were "perfect". No residual oils or other contaminants were found, and there was no damage to the electrical wiring or casings.

References:

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Recent Applications of HCFC-225 in Japan

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1. Introduction

HCFC-225 is an environmentally sensible alternative to CFC-113, perfluorocarbons and other hydrochlorofluorocarbons with high ODP values, in various industrial cleaning applications. Asahi Glass has commercialized HCFC-225, that is a mixture of two isomers (HCFC-225ca and HCFC-225cb), named Asahiklin® AK-225[1,2]. AK-225 is very similar to CFC-113 in physical properties, material compatibilities, and cleaning performance and widely used in precision cleaning.

AK-225 forms azeotrope-like mixtures with alcohol and other solvents and they are suitable for defluxing applications. AK-225AES that is an azeotrope-like mixture of AK-225, ethanol and stabilizers can be used for many defluxing applications. AK-225T and AK-225ATE were developed to solve a white residue problem which occasionally forms on printed circuit boards cleaned with AK-225AES[3]. AK-225T is a mixture of AK-225, ethanol, hydrocarbon and stabilizers. AK-225ATE is an azeotrope-like mixture of AK-225, ethanol, trans-1,2-dichloroethylene and stabilizers.

In this paper, the wide range of applications of HCFC-225 and its blends especially in Japan will be reviewed. Typical cleaning applications, parts to be cleaned with HCFC-225, cleaning procedures, and the applications for a carrier solvent will be presented.

2. Demand and Application for HCFC-225

Figure 1 shows the annual sales quantity of HCFC-225 for five years. Asahi Glass began to sale HCFC-225 in 1991. The demand rose up rapidly in 1992 and has increased continuously. Seventy-five percent of the quantity is used in Japan. Remaining portion is used in the U.S. and Asia.

Figure 2 shows a breakdown of AK-225 usage based on the kinds of blends. About fifty-five percent of the usage is neat AK-225 that is a mixture of two isomers. Most of the remainder is AK-225AES that is a mixture for defluxing application. AK-225 is used as a precision cleaning agent for metal parts, plastic parts or hybridized ones. AK-225 is recently used as a rinsing and drying agent for parts cleaned with other alternative cleaning agent to CFC-113 and methyl chloroform. It is also used as a carrier solvent and one for chemical reactions. AK-225AES, AK-225AE and AK-225T are used as a defluxing agents for printed circuit boards, hybrid circuits made of ceramic substrates and rotors of motors.

3. Applications of AK-225 Combined with Other Cleaning Agents

Miniature bearings are precise parts required size accuracy and high reliability. In the manufacturing process, various processing oils are used for cutting and polishing. After assembling the bearing, the oils should be cleaned completely and an anti-rust agent would be coated them simultaneously. A bearing manufacturing company uses AK-225 and hydrocarbon cleaning agent for cleaning and coating of anti-rust agent.

Figure 3 shows the process flow chart of the cleaning and coating procedure. In the 1st to 3rd sumps, assembled bearings are cleaned with a hydrocarbon solvent under ultrasonic oscillation. The solvent is removed by air-blow in the 4th sump. In the 5th sump, the bearings are immersed in AK-225 and the hydrocarbon and oils are cleaned completely under ultrasonic osillation. There is AK-225 containing a few percent anti-rust agent in the last sump. The bearings are immersed in the sump and the agent is coated on their surface.

Hydrocarbon will accumulate in the 5th sump. It is important to control the content of the hydrocarbon in AK-225 to avoid a fire accident. This mixture has no flash point unless the hydrocarbon content exceeds fifty percent. To avoid a hydrocarbon brought out into the 6th sump which cause contamination of the bearing surface, the content of hydrocarbon in the 5th sump should be maintained below twenty percent. The content can be monitored by the relationship between specific gravity and hydrocarbon content shown in Figure 4. AK-225 is used while the specific gravity is monitored and while AK-225 is recycled continuously with distiller set in the system.

New applications where AK-225 is used with other solvents as mentioned above are increasing in Japan. Typical another application is as follows: Parts are cleaned with hydrocarbon and then rinsed with AK-225 vapor to remove the hydrocarbon adhered on their surface. In other application, parts are cleaned with aqueous or semi-aqueous cleaning agent and then rinsed with water. After rinsing, water adhered on the

surface is removed with alcohol, then the alcohol is removed with AK-225. In these applications, customers firstly used these "not-in-kind" cleaning agent other than AK-225 to replace CFC-113. However, they have adopted AK-225 additionally as a rinsing and drying agent to solve drying and/or water spot problems.

In these applications, the content of hydrocarbon or alcohol can be monitored with the specific gravity or boiling point of the mixture. Figure 5 shows the relationship between the content of isopropyl alcohol and boiling point. The mixture will become inflammable if greater than 20% by weight alcohol concentrates in the mixture. It is necessary to maintain the alcohol content at or below 10% by weight by monitoring the boiling point. The content can be monitored by specific gravity of the mixture like Figure 4 shown above.

The usage of AK-225 combined with other cleaning agent as mentioned above has the following advantage. Usually the combination is used when the solvency of AK-225 is insufficient for the cleaning application. In such cases other cleaning agent is used for cleaning and AK-225 is used as a rinsing and drying agent. This process makes cleaning and drying time shorter than the one using only other cleaning agent. It also can be used as precision cleaning process.

4. Defluxing of Printed Circuit Boards for Automobiles

High reliability and durability are required for printed circuit boards (PCBs) installed in automobiles. Therefore, many of them are usually coated by resin. The manufacturing process of the PCBs consists of soldering electronic devices, cleaning and coating. It is necessary to clean them in a short time because a huge number of the PCBs are produced.

There are many manufacturers using AK-225AES for defluxing these PCBs. Most of them use fluxes and solder pastes for AK-225AES to shorten cleaning time and improve cleaning efficiency. Fluxes and solder pastes developed for AK-225AES are shown in Table 1.

A customer uses AK-225AES with three-sump type cleaning equipment shown in Figure 6. The procedure consists of immersing PCBs into warm solvent with the temperature of 45 to 50℃, rinsing with cold solvent and drying in solvent vapor. The tact time is 15 seconds and the all procedure ends within one minutes.

Other customer uses it with vertical two-sump type cleaning equipment shown in Figure 7. PCBs are

cleaned with warm solvent (40 to 45℃) first, then rinsed with spraying of the cold solvent and dried in solvent vapor. The tact time is ten seconds or more and the procedure ends within one minutes.

These customers do not clean all PCBs which they cleaned with CFC-113 a few years ago. They evaluate the necessity of cleaning PCBs and use AK-225AES only in the applications where it is essential. They also use AK-225AES with recovery and/or distillation equipment to reduce the consumption and solvent emission.

5. Special Cleaning and Other Applications

Recently AK-225 is used in special cleaning and non-cleaning applications. In such applications, AK-225 is used as a substitute for CFC-113 or other solvent. A new application that has never seen before in the applications of CFC-113 has also emerged.

Such special cleaning includes: refrigeration cycle cleaning where CFC-11 was used, and liquid oxygen cleaning for aerospace and iron manufacturing where carbon tetrachloride was used.

AK-225 is used as carrier solvents of silicones which is coated on a needle of a syringe, and of lubricant which is coated on a hard disk. Furthermore, it is used as a solvent for chemical reaction.

A few thousands metric tons of CFC-113 per year has been used in dry cleaning for garments in Japan. A certain amount of CFC-113 has been replaced by AK-225 gradually in this application for the last few years. New dry cleaning equipment designed for AK-225 is on market from several equipment manufacturers. Soap for AK-225 is also available in Japan.

6. Conclusion

CFC-113 was banned at the end of 1995 in non-Article 5 countries based on the Montreal Protocol. Solvent use of HCFC-141b was banned at the end of 1996 in the U. S. based on the SNAP program. The use will be frozen in 2,000 and be phased out by 2,010 in Japan based on the guideline of MITI. AK-225 is an HCFC and considered as a transitional alternative which will be phased out by 2,020 based on the Montreal Protocol. However, as described in the report of the fifteenth meeting of the open-ended working group of the parties to the Montreal Protocol[4)], for certain AK-225 applications the use of this chemical remained important, in view of the lack of appropriate alternatives with good technical or environmental performance.

Such applications would include cleaning parts that are required high reliability, and newly developed ones that require the performance of AK-225 essentially.

References

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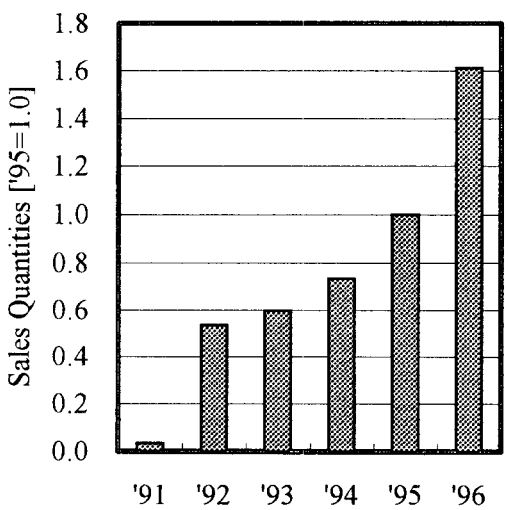

Fig. 1. Annual Sales of AK-225

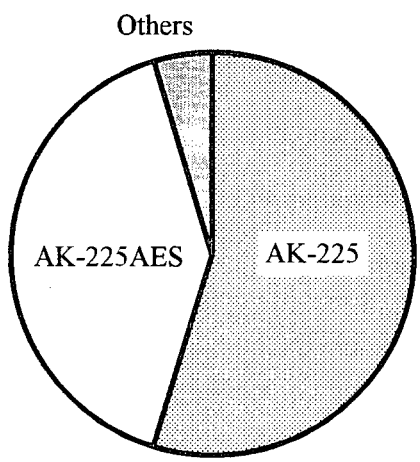

Fig. 2. Breakdown of AK-225 by products

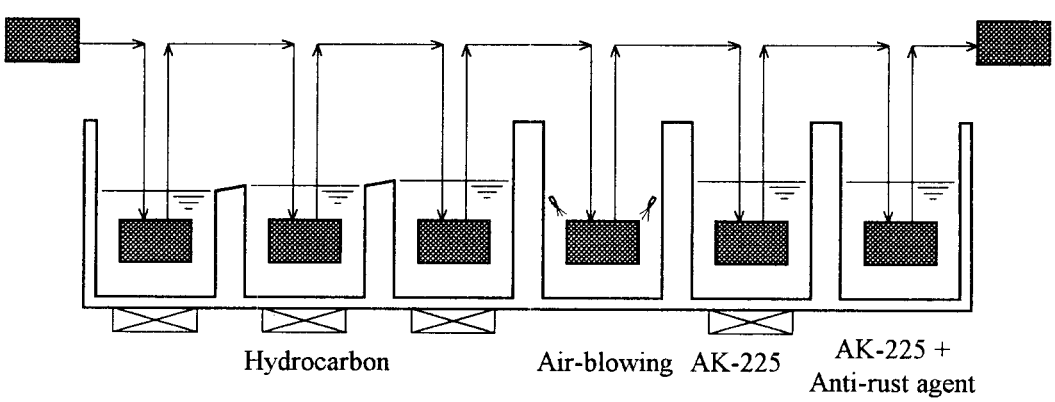

Fig. 3 Schematic Diagram of six-sump type cleaning equipment used by bearing manufacturer

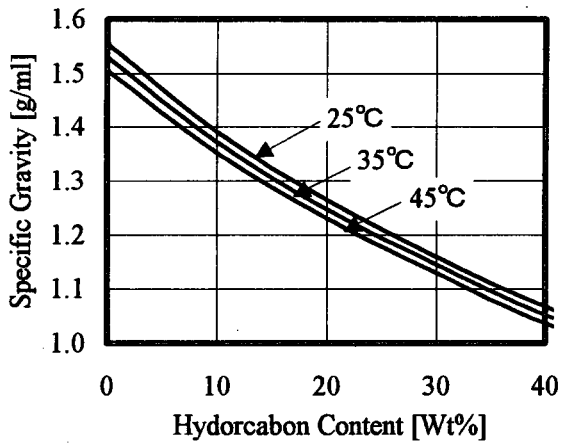

Fig. 4 Relationship between content of hydrocarbon and specific gravity

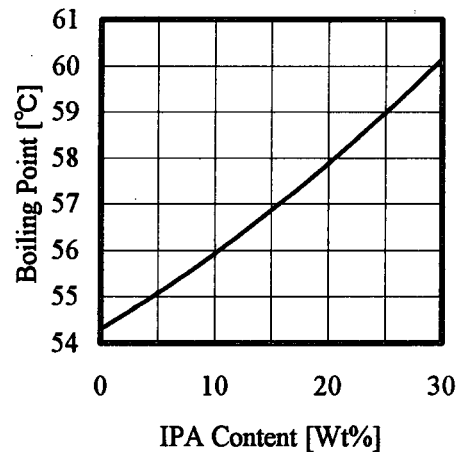

Fig. 5 Relationship between content of IPA and boiling point

Table 1. Fluxes and Solder Pastes for AK-225AES

Manufacture	Flux	Solder Paste
Alphametals	SM4592C-10T RM615-15 R5186	SR-9100-39
Asahi Chemical Res.	AGF-200FZ	—
Harima Chemicals	—	F6, F16, F27 Types
Koki	JS-64-ND-3	SE4-A228
Nihon Handa	—	RX-463-AK-3 RX-462-AK-3
Nihon Superior	NS-829	SM63RA-FMQ7S
Senju	PO-4003-K3 PO-F-210-K4 SR-210-K2	OZ 63-606F-AA-10.5 OZ 2062-606F-AA-10.5 OZ 63-633F-42-10 OZ 2062-633F-42-10
Tamura	CRF-225-20	SQ-1040AK-7 SQ-1030AK-7 SQ-2030AK-7

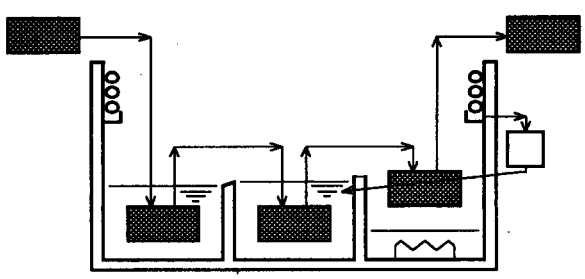

Fig. 6 Schematic Diagram of three-sump type cleaning equipment

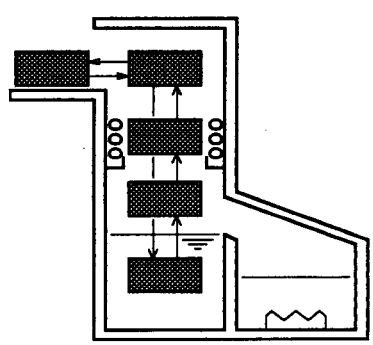

Fig. 7 Schematic Diagram of vertical two-sump type cleaning equipment

Precision Cleaning Using Hydrofluoroethers (HFEs)

Abstract

Sumitomo 3M has worked in the ODS replacement market for nearly a decade. Since the early 1990s, 3M sold PFCs to the Japanese cleaning market as alternatives to ODS solvents. During this time, a good relationship was built with equipment manufacturers and customers, and soon 3M gained a clear understanding of the customers' requirements for fluorinated solvents.

The method by which parts are cleaned by hydrocarbon solvents and fluorinated solvents was developed by 3M and other companies. It is now established as one of the major cleaning systems, and it is a well-recognized co-solvent system as well.

3M recognized that PFCs had a long atmospheric lifetime and contributed to global warming. In response, we sought to introduce new fluorinated solvents to replace the PFCs and expand the use of our products in the cleaning market. Sumitomo 3M introduced HFE-7100 end of last year. Since that time, we have introduced HFE-7100 into the Japanese cleaning market. We believe that HFE is a better product than PFC in a co-solvent system and in some cases feel it can clean a part all by itself. Some technical data, which will be discussed, indicate that HFE cleaning systems are better than the original systems that useed ODS solvents. In addition, a few examples of actual HFE cleaning applications by Japanese customers will be presented.

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Abstract

High Performance Metal Cleaning Using Liquid CO2 and Surfactants

By

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In the late 1980s the world mandated the end to production of substances that deplete the Earths Ozone Layer. These substances include chlorinated solvents which are typically used for industrial surface cleaning. The use of CO_2 as a cleaning compound offers potentially major benefits to the elimination of solvents as an atmospheric pollutant. The key to CO_2's application as a surface cleaner however its enhancement to permit the removal of a board range of surface contaminents. Recent developments in CO_2 compatible surfactant chemistry presentrs the possible solution to make CO_2 a comprehensive solvent suitable for general and precision surface cleaning.

This paper discussed the scope of CO_2 cleaning and the benefits that the new surfactant developments will give to CO_2 as a potential new surface cleaning technology.

High Performance Metal Cleaning Using Liquid CO_2 and Surfactants

by

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Introduction

The landmark treaty, the Montreal Protocol signed in 1987 and the U.S., Clean Air Act of 1990 mandated the end to production and use of substances that deplete the Earth's ozone layer, sometimes called ozone depleting substances (ODSs). Since that time the developed industrial world has been struggling to find suitable and effective alternatives for these critical industrial chemicals. Two of the more widely uses ODS are the chlorinated solvents 1,1,1 trichloroethane (TCA) and trichloroethylene (TCE): used for surface cleaning of metal components and parts.

Many industrial operators have dealt with the challenge of surface cleaning by pushing the problem off on to their suppliers, by utilizing 'no-clean' options where possible, and to a large extent by attempting to find workable aqueous cleaning processes. While much improvement has been made to the aqueous cleaning technology, from improved detergents, to new agitation techniques, it is clear that a growing number of users are still looking for solvents that performs like the chlorinated solvents TCE and TCA. One potential option, still in the developmental stage, is the use of carbon dioxide (CO_2) in either liquid (LCO_2) or the supercritical ($scCO_2$) state. These two states differ only in their containment pressures. CO_2 is a plentiful, non-ozone depleting compound, that is non-toxic, non-flammable, easily recyclable. Unfortunately, CO_2 alone in either state is not capable of precision cleaning for most applications without some type of enhancement to improve its solvency capability.

Background

The solvency capability of CO_2 has been known and used in the food processing industry and in wastewater treatment for a number of years. Since the early 1980s, research has been underway to investigate the use of supercritical carbon dioxide ($scCO_2$) as a solvent substitute in the polymerization of hydrocarbon monomers. This work also generated in interest on the potential use of CO_2 as a surface cleaning agent. The use of supercritical carbon dioxide, however, has not provided a totally satisfactory solution by itself. Since it is not a true liquid supercritical CO2 does not process the capability that a liquid system might provides in washing the surface and to allow removal of particles from the surface that is being cleaned. For cleaning

beyond removal of light oils it has been found to be generally ineffective. Even LCO2 does not provide a significantly greater surface cleaning capability other than for general surface cleaning.

Beginning in 1990 and working under the leadership of Dr. Joseph DeSimone of the chemistry department at the University of North Carolina at Chapel Hill and a group of 25 research colleagues at other major universities, a major breakthrough in the development of a CO_2 compatible surfactant chemistry was made.[1] The research to polymerize hydrocarbon monomers in $scCO_2$ led to the development of a group of unique CO_2 compatible phillic surfactants. The key to polymerization and to surface cleaning is the surfactant used which adds functionality and enhances the efficiency of the solvent. This development of a class of CO_2 compatible surfactant results in significant improvements in the potential of CO_2 as a solvent and thus as a cleaning agent. This work was supported by the U.S. EPA and a consortium of eight chemical companies including DuPont, Hoechst Celanese, Eastman Chemical, General Electric, Xerox, Air Products, BF Goodrich, and Bayer.[2]

General and Precision Cleaning

The key to the eventual use of CO_2 for general cleaning applications must be the improvement of its cleaning efficiency for a broad range of contaminants and surfaces. In chlorinated and aqueous based solvent systems, this is accomplished by the addition of surfactants and other additives to the chemical system. However, conventional solvents are not compatible with CO_2. The newly developed CO_2 compatible surfactants will serve the same purpose in the LCO_2 system as conventional surfactants in chlorinated or aqueous based surface cleaning system.. They will make it possible to clean the parts of contaminants that up to now have not been affected by CO_2 in any state including heavy oils greases and waxes. Being in a liquid state it will also allow for washing of the surface as accomplished in conventional liquid systems. In addition, in the liquid state the process will operate at ambient temperatures and at pressures of only 800 to 1200 psi (81×10^6 to 122×10^6 Pa), which most components can withstand without any effect on the part.

Liquid CO_2 has been shown to be capable of cleaning some metal surfaces where precision cleaning is not of great concern.[3] However without the enhancement provided by the surfactants, LCO_2 has limited application for precision cleaning. With a density close to that of water, and a viscosity more like a gas, LCO_2 has capability to remove particulate matter to a greater than that of $scCO_2$. Laboratory testing at the MiCell Technologies Inc., and at the North Carolina State University chemical engineering department, have demonstrated significant cleaning performance improvement when using LCO_2 and the new surfactants on various contaminants and material surfaces. MiCell Technologies Inc., has been licensed to produce and market
CO_2 surfactants for use in cleaning systems.

Potential of the LCO_2 Cleaning Technology

The application of LCO_2 with the surfactant additives technology is one of the most promising surface cleaning options since the development chlorinated solvent cleaners. A LCO_2 system will function similar to most present liquid systems and preserves all of the functional advantages of those systems. Since it is liquid, it can penetrate surface depressions, holes and

surface imperfections, and evaporates from the surface without leaving a residue. Finally, with the proper surfactant package, it will remove the surface contaminants removed by CFC and aqueous based solvents including oils, greases and particulate.

Carbon dioxide is not an ozone depleting compound and can be acquired as a by-product from ammonia fermentation and petrochemical processes. This eliminates a requirement to manufacture CO_2 which would add to the discharge of additional greenhouse gas into the atmosphere. The material cost of CO_2 and the surfactant package is relatively inexpensive when compared to typical chlorinated solvents or equivalent substitutes used for surface cleaning.

There are no applicable regulations to the LCO_2 process. The process residue stream could be deemed hazardous depending on the nature of the contamination removed from the surface. The Occupational Safety and Health Administration (OSHA) has guidelines for CO_2 exposure which encourages monitoring to assure CO_2 concentrations do not exceed 10 percent by volume of the average daily air intake.[4]

Conclusions

The development of a viable surfactant system for use with LCO_2 offers an environmentally safe and efficient system. The development of a compatible surfactant allows the potentials of CO_2 to be fully realized as a clean environmentally safe and non-polluting surface cleaning process . Since CO_2 can be recycled and reused, the only waste product from the process is the contaminant itself. With the development of viable surfactant additives, the major remaining developmental activity for this technology is the design of a fully integrated and economical system for industrial application.

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FORALKYL 2211 :
A New Rain-Repellent For Aerospace Applications.

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INTRODUCTION

A rain-repellent is a safety option on aircraft, which allows to maintain a good visibility in case of accidental failure of windshield wipers and intense rain during landing and the take off operations.
Since the ban of CFC 113 and the limitation of HCFC uses, the production of the current rain-repellent has been stopped. Up to now, despite numerous researches conducted in this field, no real alternative solution has been proposed.

AEROSPATIALE (AIRBUS Manufacturer), LE BOZEC FILTRATION & SYSTEMS (Aircraft Equipment Supplier) and ELF ATOCHEM (Chemical Company), added their respective competences into a partnership program to develop and validate a new rain repellent product. This new solution was defined basically as a "Drop-in" of the old product with the same technology i.e. usable with the original equipment by external spraying on the windshield, environment friendly product (zero ODP solution), non flammable, non toxic, presenting a high degree of efficiency, industrial, and with an acceptable price according to the passenger safety improvement.
The new rain-repellent solution FORALKYL 2211 presents a package similar to the previous product : i.e. a pressurized bottle located behind the pilote and capable of being released by a simple finger tip control.
Main results and properties of FORALKYL 2211 are presented here after.

FORALKYL 2211 : AN ALTERNATIVE RAIN-REPELLENT.

FORALKYL 2211 is composed of a new solvent blend which acts as a solubilizer of an active base responsible of the hydrophobic targeted effect when applied on the windshield surface.
The new solvent blend has been selected among HFC and oxygenated substances to promote the highest efficiency and preserved the non flammability and zero ODP requirements.

Temperature stability tests were carried out in order to verify the ability of the product to support the ultimate aircraft conditions. No precipitate and no modification of FORALKYL 2211 were observed in the temperature range between -55°C and +80°C.

EFFICIENCY AND PROPERTIES OF FORALKYL 2211.

FORALKYL 2211 was tested on a testing bench at LE BOZEC Technical Department's. A representative aircraft windshield including : the rain-repellent system, a sighting (cross ruling black and white) set at ca 1 meter from the windshield, a wind tunnel capable to simulate the speed at landing or take off (ca 250 km/h) and an additionnal device to produce different type of raining conditions.

A complete serie of experimentations using FORALKYL 2211 has demonstrated the high degree of efficiency of this product compared to the previous existing rain-repellent. It has been shown that FORALKYL 2211 remains efficient even after 30 minutes under the heavy rain conditions.
No dry smear effect has been observed when FORALKYL 2211 is sprayed on the surface and the visibility through the windshield appears to be immediatly equivallent to those obtained in clear and fine weather (no rain conditions).

The basic properties of FORALKYL 2211 are presented in table 1. The low surface tension combined to the low viscosity allow a good wetability of the windshield. Under raining conditions, the active material is brought immediately onto the glass with a strong dewatering effect. So, the water did not stick onto the glass and was driven off by the wind.

FORALKYL 2211 AND THE RISK ASSESSMENT.

A predictive risk assessment has been undertaken on FORALKYL 2211 following the positive applicative results.
A pressurized bottle containing 500 ml of FORALKYL 2211 is placed just behind the pilot. The internal bottle pressure is ca 5 bars.
A computer modelisation has been used to simulate a possible accidental total discharge all over the volume of the cockpit (average volume of 12 m^3). The

simulation has been done in normal ventilation conditions and in the worth case , i.e. the breakdown of the ventilation.
In both cases, the concentration of the generated vapours remain below the half of TLV of each individual chemical. In normal ventilation condition, the estimate vapour concentration was found to be 150 time less than the TLV. Furthermore, the chemicals chosen in FORALKYL 2211 showed the absence of effect, especially cardiac and central nervous effects, then it does not affect the capability of the crew.
Additionnally, if a leak of the rain repellent system accidentaly should occur, this could be easely and rapidly be detected by the pine tree flavour added to the formulation.

AERONAUTICAL EVALUATION

A serie of aeronautical tests was conducted according to the AIRBUS Industries Material Specifications (AIMS 90 100) and the relevent test methods (AITM). Tests were performed in the AEROSPATIALE Louis Blériot Corporate Center in order to verify the absence of any detrimental effect on the different material used on a aircraft (plastics, composites, elastomers, paints, sealants, metals and alloys ...).
Compatibilities of all aeronautics materials tested were found to be acceptable in the tested conditions, see table 2.
No corrosion effect or hydrogen embrittlement was observed on aluminum (2024-T3 enclad and 7075-T6), cadmium plated steel (total immersion test) and on high resistant steel.
The qualification test performed on the bottle and the system were conducted by LE BOZEC. Constant acceleration, mechanical vibration, shock, proof pressure, showed that FORALKYL 2211 does not affect the equipment.
The efficiency and the behavior of FORALKYL 2211 has been finally validated by a serie of experimentations in flights.

CONCLUSION

Important and joint effort recently developed by AEROSPATIALE, LE BOZEC FILTRATION & SYSTEMS, and ELF ATOCHEM has allowed to come up with a new rain repellent for aircraft very efficient against any type of rain from light to very heavy rain.
The new FORALKYL 2211 renamed LE BOZEC RAIN REPELLENT has been certified according to aeronautical specifications.
It has been demonstrated that this new RAIN REPELLENT is a very safe product for the environment (zero ODP) as well as for the humans health and safety (non toxic, non flammable). This new option, presented as a Drop-in of the old CFC based product, must be now find a credit for the success.
More than the respect of the Montreal protocol, the LE BOZEC RAIN REPELLENT ensures an increased level of safety on aircraft, furthermore of airlines passenger.

Table 1 : Main properties of FORALKYL 2211

Properties	Values	Methods
Density (at 20°C)	1.05	*Internal E.A. C1-223
Viscosity (at 25°C)	3.02 mPa.s	ASTM-D 445
Surface tension (at 25°C)	20.6 mN/m	NF T-73-060
Flash Point (ASTM D 3828)	NONE	ASTM-D 3828
ODP	0	

* Internal E.A. : Internal Standard of Elf-Atochem

Table 2 : Compatibility tests

TRIALS	Aluminum Alloy (2024 and 7075)	Cadmium Steel	Elastomers	Plastics	Sealants	Titanium T-A6V	Steel 35 NCD16 at 1800 Mpa	Paints 2024/A5 + Primary + Finis	Methods
Sandwich Corrosion	OK								ASTM F1100
Half immersed Corrosion	OK	OK							ISO 2812
Crazing test				OK					*Internal AS (0424130 & 0424131)
Linear Pealing					OK				*Internal AS (0426271)
Elastomers Compatibility			OK						**
Paints Compatibility								OK	ISO 2409 - ISO 1518
Stress Corrosion						OK			Internal AS - AITM 50003
Hydrogen Embrittlement							OK		Internal AS

* Internal AS : Internal Standard of Aerospatiale

** French Standards (NF) :

NF-L 17150 (silicones), 17160 (fluorocarbon), 17141 & 17142 (EPR), 17131 (chloroprene), 17120 & 17121 (NBR).

NF-T 43303 (International hardness variatio), 46113-Method A (volume variation), 46002 (variation at elongation at rupture).

Dr. Pascal MICHAUD biographie.

Pascal MICHAUD has a degree in Engineering. He got his Ph D in Chemistry in 1983 at the University of Rennes where he studied electron transfer mechanisms with Iron complexes.

He did a post-doc in Professor J.K. KOCHI 's laboratory at the University of Houston where he did some work on catalytic epoxidation of olefin with various oxygen atom donnor assisted by inorganic manganese complexes.

He joined ELF-ATOCHEM in 1985 in the Research center in Pierre Benite in France and started working in organofluorine chemistry.

He moved to the Application Research Center in Levallois in 1988 and currently is in charge of the laboratory studies on solvents application reseach for ELF-ATOCHEM, especially the substitution of CFC and HCFC.

JAPANESE TECHNOLOGY TRANSFER FOR CLEANING APPLICATIONS

Kiyoshi Hara
Japan Industrial Conference for Ozone Layer Protection

Overview

In Japan, when consumption was at its highest level in 1989, 200,000 tons of 1,1,1-trichloroethane (TCA) and 80,000 tons of CFC-113 were used. By the end of 1995, however, production of these and other ozone depleting substances (ODSs) was to be terminated. This would prove to be a significant challenge for both industry and government, both of which had agreed that the elimination of ODSs was necessary.

In early 1996, Japan's Ministry of International Trade and Industry (MITI) announced the following policies relating to ozone-layer protection:

- Early phaseout of HCFC and methyl bromide
- Elimination of TCA and CFC-113 in small- and medium-sized companies
- Establishment of CFC recovery and destruction systems
- Cooperation with developing countries on ODS elimination
- Consideration of global warming effects in the development of CFC alternatives

The Japan Industrial Conference for Ozone Layer Protection (JICOP) was established to help facilitate an early and smooth phaseout of ODSs in Japanese industries by supporting the Ozone Layer Protection Office of MITI. JICOP is a non-profit, private association representing all of the major industries that manufacture or use ODSs in Japan. As of July 1997, 57 industrial associations had become members of JICOP.

JICOP has played an important, often leading role in the phaseout of CFCs, TCA, carbon tetrachloride (CTC), and halons in Japan by educating both industry and the public on the need to protect the ozone layer. JICOP accomplished this in part by (1) encouraging industries to take voluntary action to phase out ODSs expeditiously, (2) organizing a number of Ozone Layer Protection Promotion Seminars and Campaigns, and (3) publishing manuals for preventing ODS emission, bulletins on ODS free technologies, and periodicals covering the latest ODS phaseout technologies.

JICOP also has contributed significantly toward the worldwide phaseout of ODSs by promoting the transfer of essential technologies to developing countries. For example, in cooperation with the Japanese government we organized 40 days of group training courses on methods of reducing ODS use. It also is important to note that since 1990, a total of 124 government officials and technicians from 30 different countries have been invited to Japan as part of our technology transfer efforts. In partnership with MITI, the U.S. Environmental Protection Agency, and other organizations, JICOP has co-organized seminars on alternative cleaning technologies in South-East Asian countries since 1992 in Thailand, Malaysia, Singapore, Indonesia, Vietnam and Philippines.

In April of this year, UNEP/IE requested that MITI and JICOP publish Japanese case studies on successful ODS phase-outs. This report is to be published by September 1997 and distributed to the delegation of the Ninth Meeting of the Parties to the Montreal Protocol. Nineteen case studies will be discussed, nine of which are from the cleaning sector. This presentation consists of brief descriptions of each of these nine case studies.

Vacuum Cleaning and Drying Technology for Difficult-to-Clean Precision Metal Parts

Background

Seiko Epson Corporation used CFC-113 and TCA for cleaning and drying processes involving circuit boards, precision metal parts, plastic parts, and semiconductors. The company evaluated alternative methodologies in the following order of priority:

1. Elimination of cleaning or drying process.

2. Conversion to aqueous cleaning when it was impossible to eliminate either the cleaning or drying process.
3. Use of solvent cleaning when conversion to aqueous cleaning was not possible.

In 1994 Seiko Epson introduced a vacuum cleaning and drying technology for difficult-to-clean precision metal parts.

Alternative Technology

The new vacuum cleaning and drying system uses ultrasonic waves while simultaneously reducing pressure in the system. The cleaning process agitates the solvent with gas bubbles, which enable smooth stirring and substitution, and cavitation is strengthened by the ultrasonic waves. As a result, the parts being washed are vibrated (Figure 1).

Advantages

- The cleaning quality is high because the metal parts are washed using pure vapor in the final rinse process.
- This method applies sufficient heat to the parts in a short time. In this case, the parts are heated by hot vapors (120-130°).
- It is safe from the perspective of both health and the environment because the drying process is carried out in a closed chamber.

Economic Benefit

The annual volume of detergent used is 2,400 liters in a new system that uses hydrocarbons, compared with the 6,300 liters of a conventional TCA system. Annual detergent cost is $8,200 U.S. in new system and $22,000 in a conventional system.

Previously, using conventional TCA cleaning methods, 0.15% of metal parts rusted after cleaning due to atmospheric moisture contamination of the TCA. The new method reduces this problem by 50%. The cycle time remains the same as the previous solvent-cleaning system.

Heat Exchange Cleaning

Background

TCA was previously used as a cleaning agent to remove processing oil employed in the manufacture of heat exchangers of air conditioners. Toshiba adapted a volatile oil as the processing oil and substituted a drying process for the cleaning process.

Alternative Technology

Volatile processing oils have low viscosities and poor processing characteristics, and thus use of volatile oils in the processing of fins and U-shaped pipes, which are key components of heat exchangers, poses difficulties. To overcome these difficulties in the processing of fins, the die structure for processing was improved by modifying materials and dimensions, and an oil supply mechanism was added as well.

Development of Facilities

Special drying equipment was developed for the removal of volatile oil. This hot air-blow drying equipment, which uses indirect heating, can produce temperatures of 150° for 10 minutes. Volatile oil is a highly combustible, hazardous material. Therefore, as a safety measure, a gas-concentration sensor and exhaust equipment were installed. For environmental protection, exhaust treatment equipment using catalytic combustion was installed. As a result, exhaust gas concentration is maintained at less than 50 ppm.

Economic Benefits

The investment cost for the new equipment is approximately $3.7 million. However, the use of TCA is reduced by 570 tons/year, resulting in a $1.3 million raw material cost savings.

Water-Based Cleaning System for Ball Bearings

Background

Miniature ball bearings need to be accurate in size, silent, reliable, and long lasting for applications such as computer peripherals and aircraft instruments. Thus, in the manufacture of these bearings, the cleaning process is the most important factor. In the past, large volumes of CFCs and TCA had been used for cleaning purposes.

Alternative Technology

Minebea Co., Ltd., successfully developed an ODS-free technology using a water-based cleaning system that does not employ ozone-depleting substances.

Water is the predominant cleaning medium. Although water does not have the ability to dissolve oil stains, it does have the maximum solubility for electrolytic organic and inorganic salts, and it excels in dissolving alcohols, proteins, carbohydrates, etc. Nevertheless, problems such as rusting have prevented its use in the field of industrial cleaning, despite its excellent properties.

Minebea developed a cleaning system using water with a low concentration of dissolved oxygen, achieved via a deoxidizing device with a vacuum degassing system to prevent rusting during immersion (Figure 2).

Advantages

1. It eliminates the use of ODSs.
2. It delays the rusting process in soaking by using water with low dissolved oxygen.
3. It enhances the ultrasonic energy because the water from which oxygen and nitrogen have been removed increases the cavitation effects of ultrasonic waves.

Economic Benefits

This system requires initial investment for the installation of facilities for the purification and treatment of waste water.

Minebea invested $45 million for these facilities. This water-based washing system does not incur the cost of solvents but does bear the cost of manufacturing purified water and waste-water treatment systems. Its operating costs are approximately the same as those for traditional ODS-based systems.

Alternative Precision and Electronics Cleaning Technology

Background

Asahi Glass Co., Ltd., (AGC) developed ASAHIKLIN AK-225 (AK-225), which is an environmentally acceptable, transitional hydrochlorofluorocarbon (HCFC) designed to replace CFCs, PFCs, and other HCFCs with high ODP values. It has a substantially lower global warming potential than PFCs and HFCs, as well as an extremely low ODP. AK-225 is thermally stable and nonflammable. Its selective solvency, physical properties, and ability to form azeotropes made AK-225 ideal for general, precision, and electronics cleaning.

AK-225AES is an azeotrope-like mixture of AK-225, ethanol, and stabilizer, and was developed as a defluxing agent.

Alternative Technology

Miniature bearings are precision parts, and their manufacture requires size accuracy and reliability. In the manufacturing process, various oils are used which must subsequently be removed. In addition, the bearings must be coated with an anti-rust agent. Thus, Asahi Glass developed a precision cleaning process and an anti-rust agent coating.

AK-225 is used as a substitute for CFC-113 in the precision cleaning process. The cleaning equipment in the process has six sumps. In the first three sumps, the bearings are cleaned by a hydrocarbon solvent, and the solvent is subsequently removed by air blowing in the fourth sump. In the fifth sump, the hydrocarbon solvent and the oils are removed completely by immersing the bearings in AK-225. The final sump contains AK-225 and an anti-rust agent. By soaking the bearings, the application of the anti-rust coating is done easily. AK-225 is the only solvent that can be used in this process in place of CFC-113.

Advantages

Significant and long-lasting reliability is required for printed circuit boards (PCBs) installed in automobiles, and thus many of them are coated with resin. The manufacturing process for these PCBs is followed by the soldering of electronic parts, cleaning flux, and coating. It is necessary to clean and dry parts in a short time due to the large production volumes. In addition, alternatives to CFC-113 for this process are extremely limited due to effects on the electronic parts.

There are many PCB manufacturers that use AK-225AES for defluxing. The cleaning procedures are quite similar to those for mixtures of CFC-113 and alcohol. The tact time (dipping time in each sump) is 15 seconds; and cleaning and drying end within one minute. AK-225AES can be used in existing cleaning equipment with only minor modifications.

Economic and Technical Advantages

1. Existing cleaning equipment for CFC-113 can be used with only minor modifications.
2. The cleaning procedure and time do not need to be altered.
3. Rinsing and drying after cleaning are not necessary.
4. Reduction in the cost of cleaning can be realized by minimizing solvent emissions through the following methods:

    - Modification of cleaning equipment to decrease the amount of consumption.
    - Installation of a solvent-recovery system and/or a solvent- recycling system using distillation.

Water-Based Cleaning for Shadow Masks and Peripheral Parts for Cathode Ray Tubes

Background

Mitsubishi Electric Corporation, a cathode ray tube manufacturer, historically used a large amount of TCA to clean shadow masks and their peripheral parts manufactured by pressing.

These solvents were used during immersion or sonication cleaning because of their penetration characteristics. Mitsubishi realized the necessity of identifying a non-flammable, aqueous detergent that was safer than other substitute detergents. Mitsubishi also sought a detergent that had rust-inhibition qualities and left little residue on parts prior to the heat treatment in the subsequent process.

Dai-ichi Kogyo Seiyaku Co., Ltd., a detergent manufacturer, developed a new detergent that met Mitsubishi's requirement. This detergent has been adapted for Mitsubishi's cleaning process and has replaced its conventional cleaning equipment because the cleaning mechanism of the aqueous detergent is different from that of

TCA. The new cleaning equipment, manufactured by Kanken Techno Co., Ltd., has been adapted for this aqueous detergent.

Alternative Technology: Detergent

The new detergent has temporary rust-inhibition abilities for metal parts due to the presence of organic alkali as one of the components of the detergent.

It is easy to remove metal parts while rinsing, and it has no influence on metal parts in subsequent processes, even if the detergent remains on the metal parts because it does not contain alkaline metal salts. A smaller amount of detergent is used because it is diluted with water in a concentration range of 5-10%.

Alternative Technology: Cleaning Process

The cleaning system works with an aqueous detergent solution sprayed from a nozzle onto the surface of metal parts (i.e., shadow masks) at a low pressure. It is possible to maintain the same cleaning ability as that of TCA by controlling the spray pressure and the discharge amount of detergent solution. Any accumulated working oil in the cleaning tank is removed by oil-water separation equipment, and thus the detergent solution can be used for several months without renewal. This process requires lots of water to rinse the detergent. The amount of rinsing water can be reduced by regenerating it and by reducing the amount of detergent solution brought from the cleaning tank.

It is important to maintain a low detergent concentration in the rinsing water. In order to preclude any influence on metal parts in subsequent processes, electric conductivity is an easy method of determining the detergent concentration.

Advantages

1. The detergent use is approximately one third of that of TCA.
2. The total cost of detergent used is approximately one half that of TCA.

Cleaning Pressed Parts Made of Zinc Coating Sheet Iron

Background

Canon Inc., as part of their environmental policy established in 1989, decided to discontinue using ozone-depleting solvents. Thus an evaluation of alternatives to CFC-113 and TCA was needed.

Alternative Technology

Canon decided to select alternatives for TCA from the group of hydrocarbon cleaning solvents because hydrocarbons had suitable solvency, low cost, and fewer environmental problems such as ozone depletion and less water and soil contamination.

Canon adopted the hydrocarbon cleaning solvent "NS Clean TM" produced by Nikko Petrochemicals Co., Ltd. The company also decided to adopt the No. 3 petroleum (classified by a flash point of 70°) defined by the Japanese Fire Service Law because of fire safety issues. The cleaning capacity of NS Clean is almost equal to that of TCA, and the drying speed is the highest among the No. 3 petroleum solvents with similar flash points.

NS Clean is composed of a single hydrocarbon component, so it has a high drying efficiency and a high flash point. It does not leave any non-volatile residues because of its high purity. It has low odor and low toxicity, and it is non-corrosive with respect to various metals and plastics. Therefore, metal parts could be cleaned easily in polypropylene baskets.

The cleaning system is a fully automatic machine with three baths heated to 50° (20° lower than the flash point) in order to satisfy the requirements of both solvency and safety. The drying section consists of two stages. The first stage uses an up-flow of hot air heated by steam and the second stage uses down-flow. The vacuum distillation unit (80 liters/hour) also is equipped for the recycling of the waste solvent. The purity of the recovered solvent is 99.9%, and the recovery rate is 98%. Because the waste solvent from the bottom of the distillation unit is burned as a fuel for the steam boiler, no industrial waste is produced (Figure 3).

Economic Benefit

Using conventional technology, these two cleaning processes consumed three tons of TCA per month, whereas the consumption of NS Clean is only 1,650 liters per month. The running cost savings is over $87,000 per year, and the total investment is approximately $565,000.

Advantages

1. Complete elimination of ODSs.
2. Elimination of industrial waste.
3. Increase in production because the same polypropylene basket can be used without placing the parts into another basket.

Using a Semi-Aqueous Solution to Clean Printed Circuit Boards

Background

CFC-113 has been used in the past for flux cleaning before new regulations prohibited its production. As it has adverse effects on the environment, it should be replaced with suitable alternatives.

Some semi-aqueous or hydrocarbon detergents are promising as substitutes for CFC-113 in flux cleaning, but they are hazardous because of their flammability. For this reason, a mechanism for preventing explosions was required.

Nihon Kakohki Kogyo has developed a non-explosive cleaning machine using a semi-aqueous solution.

Alternative Technology

In order to prevent explosions from flammable detergents, a closed explosion-proof cleaning tank is used. In addition, an inert gas atmosphere is used in which boards are cleaned in the detergent by jet. After the boards are cleaned they are transferred to another tank for rinsing by a water conveyor that reduces the adherence of flammable detergent. In the rinsing tank, the detergent is removed completely, and boards then are dried by hot air. This system is referred to as a serial-continuous cleaning method. To avoid leakage of flammable detergent and nitrogen to the outside of the washer, there is a waiting section with double doors at the loading position. The double doors are not opened at the same time, thereby preventing the inert gas in the washer from flowing out directly. Finally, parts with blind holes (which could not be cleaned well by horizontal placement) are placed vertically so they may be cleaned by being dipped in water and sprayed.

Economic Benefit

The amount of investment varies, depending on the size of the machine. An example is as follows:

Work size: Maximum 500×500×30 mm
Tact: 3 minutes/basket
$570,000 excluding a waste-water treatment system ($220,000)

Approximately $240,000 is a realistic figure for a simpler specification.

Cleaning Machine for Lead Frames on Integrated Circuits

Background

A lead frame is a thin plate of a large-scale integrated circuit (LSI). In order to eliminate the use of CFC-113 as a cleaning agent in the manufacture of lead frames, Apic Yamada selected the automatic vacuum cleaning machine designed with a totally new concept by Kimura Chemicals Plants Co., Ltd.

The new technology is capable of cleaning and drying lead frames continuously and automatically by using a hydrocarbon solvent as the cleaning agent.

Alternative technology

In large quantities, LSIs are very difficult to clean and dry completely because it is necessary to clean them in piles to prevent deformation. Good cleaning is possible, however, when the lead frames are cleaned in a vacuum. In addition, vertical vibration is applied for further improvement. The hydrocarbon solvent has a boiling point of 172° and a flash point of 53°.

The new equipment can clean parts automatically and continuously. First, the parts are loaded onto the machine from the inlet and cleaned in a preliminary bath, then they are transferred to a second bath and cleaned under vacuum. Subsequently, the parts are transferred to a drying room where they are dried under vacuum. Finally, the parts are cleaned and dried repeatedly in third and fourth bath (Figure 4).

Advantages

This technology can clean and dry a large number of lead frames (55×250×0.5 mm) at a rate of approximately 180,000 pieces for each 8 hours in a short processing time (less than 12 minutes). The pieces are placed on a large tray automatically and continuously. The productivity of this technology is about six-fold greater than that of the previous one.

Cleaning Color Picture Braun Tubes With Hot Water

Background

Toshiba Metal Parts Co., Ltd., manufactures 300,000 pieces per month of mask frames and inner shields of color picture Braun tubes used for televisions and computers. In the past, Toshiba cleaned these mask frames and inner shields with TCA.

Toshiba has evaluated various solvents and technologies for alternatives to TCA. In particular, it wanted to adopt technologies both benign to the environment and economically advantageous. Thus, in cooperation with Organo Corporation, one of the leading water-treatment companies in Japan, Toshiba Metal developed a cleaning system that uses hot deionized water

Alternative Technology

Toshiba formerly used TCA to remove the oil used in its pressing step in the manufacture of its mask frames and inner shields. The company has since replaced TCA with hot deionized water.

As water is deionized or purified, the dissolution power of water increases, and thus press-working oil or any other contaminants on the metal parts can be dissolved and washed away more easily. In addition, as the electric resistance of the deionized water is high, the objects to be cleaned are less electrostatic and contaminants are prevented from adhering to them.

As oil viscosity decreases with increasing temperatures, the oil adheres less to the parts being cleaned, thereby promoting the dislodging of oil from the metal surfaces. Oil removal is promoted further by ultrasonic cavitation, and diffusion is enhanced by spray injection and recirculation of the cleaning agent (deionized water).

It takes 80 seconds for mask frames to be transferred from the cleaning section to the end of the drying equipment. The cleaning wastewater is sent to an oil-water separation unit, followed by a deionized-water recovery system called "AQUACON."

The oil separation unit is a filter charged with an oil coalescer which causes floating and emulsified oil to agglomerate (coalesce) and be accumulated in the upper portion of the filter vessel. The oil thus accumulated is discharged when its level in the filter vessel has reached a present level detected by an oil sensor. The effluent from the coalescer filter is then sent to a pretreatment filter, as well as an ion exchanger vessel to remove suspended solids, residual oil, and metal ions, respectively. Next, the rejuvenated deionized water is sterilized (Figure 5).

Advantages

This alternative technology contributes not only to the prevention of ozone depletion but also to various improvements in the workplace environment as listed below:

1. No waste generated except for sludge to be carried offsite for disposal.
2. No emission of odor.
3. Workers are not exposed to toxic and carcinogenic substances.
4. No pollution of soil and water bodies with TCA stored or used.

Economic Benefit

The cleaning cost of this method is reduced by approximately one third of that of the TCA method.

* * * * *

For further information on any of these case studies, please contact JICOP as follows:

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Fig.1

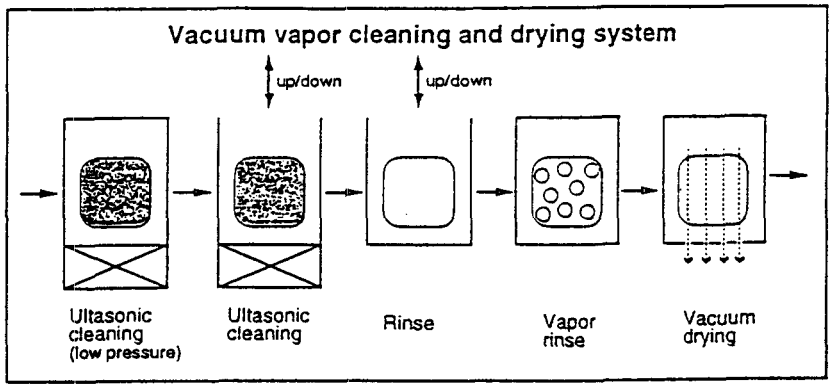


Fig.2

Diagram of water based cleaning system

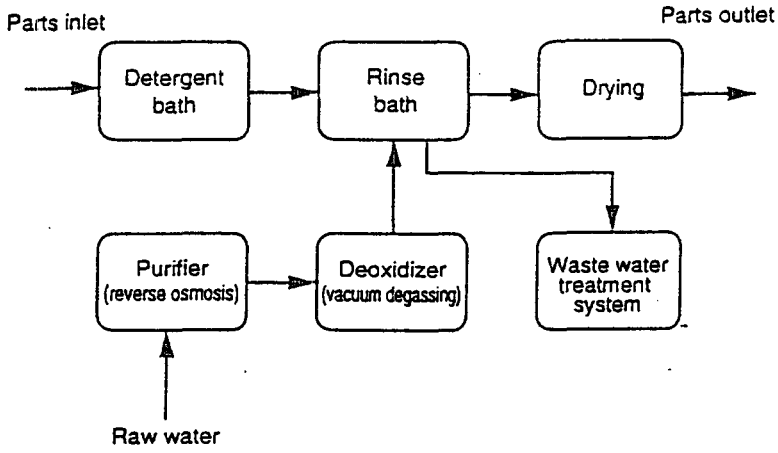
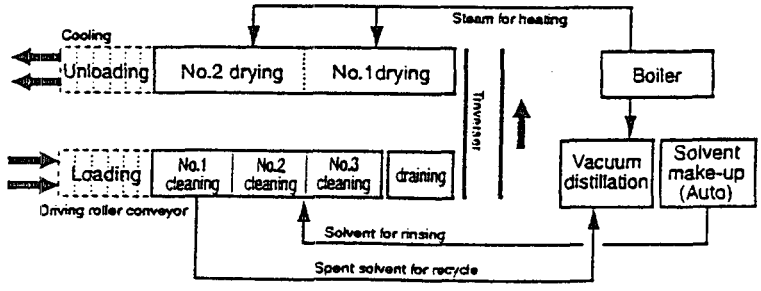


Fig.3

New cleaning technology (Full-automatic large cleaning machine)



No.1 cleaning: Dipping in NS clean with ultrasonic, vertical swing and/or jet flow.
No.2 cleaning: Dipping in NS clean with ultrasonic, vertical swing and/or jet flow.
No.3 cleaning: Dipping in NS clean with vertical swing and/or jet flow.
No.1 drying: Up flow air (110°C) heated by steam.
No.2 drying: Down flow air (120°C) heated by steam.

Fig.4

Flow of lead frame cleaning machine

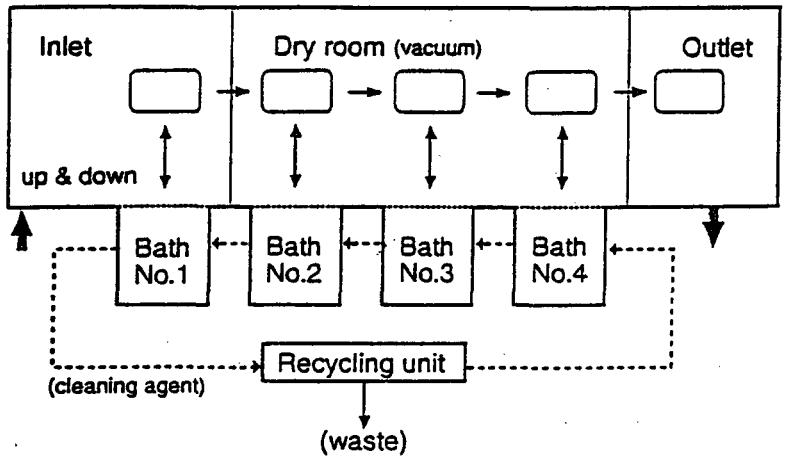
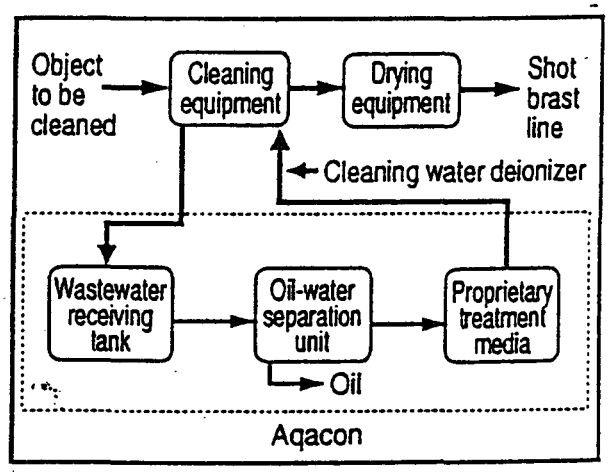


Fig.5



Flow diagram for cleaning mask frame using hot deionized water

The Chlorinated Solvents NESHAP - Results to Date, Recommendations, & Conclusions

by John B. Durkee, II, Ph.D., PE

ABSTRACT
This paper describes the history, methodology, and impact nearly through the compliance date of the NESHAP for chlorinated solvents. This rule "broke the mold" because it: spoke against "political correctness" and validated use of solvents; was "user friendly" because the EPA gave users so many ways to comply; and yet was not a complete break from the past because enforcement was based on an old-style punitive approach.

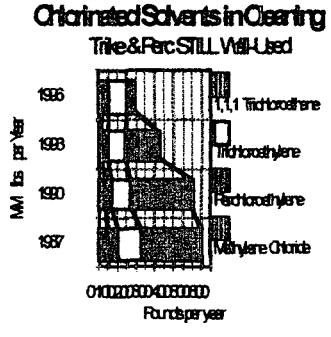
Was this rule a success? Were users happy about the "user friendly" rule? Did the enforcement approach have an effect? The answers revealed in this paper are that --many users have complied with it's provisions; yet we'll present evidence that suggests that success hadn't happened through 1996. Users were presented with a smorgasbord of choices for compliance, yet they are seen being as confused as a kid with a $5 bill in a candy store. The EPA wanted to make it simple and easy for users to make the choices which most reduced emissions, yet the vast majority have chosen other approaches because of the enforcement basis in the rule.

BACKGROUND
This standard was one of the enabling events that spawned what many have described as the "renaissance of solvents." The EPA spent several years in development, and it was their method of validating use of solvents as cleaning agents.

Simply, the NESHAP for chlorinated solvents said that it was OK to use solvents about which there are environmental or health concerns — if emissions from cleaning operations were controlled in certain ways. The NESHAP didn't speak about solvent concentrations being below certain limits — that's OSHA's (and your....) responsibility.

In addition to the normal problems associated with complying with environmental regulation, this NESHAP brought one more problem — it wasn't simple.

Figure 1



- The EPA had to allow US industry the opportunity to have a great deal of flexibility in choice about compliance. US industry made it plain they demanded that choice in their comments about the initial draft of the NESHAP they provided to the EPA. The EPA met their aim. Unfortunately, the breadth of choices lead to confusion — similar to a small boy in a candy store with a $5 bill.

- The EPA had to make enforcement simple and low-cost. They met that aim — because compliance involves self-monitoring and reporting.

- The EPA had to make it easy for US industry to make the "right" choices — those which allowed less emissions of HAPs. Again, they met that aim by creating the idling and total emission methods. Unfortunately, very few users ave chosen those methods because the self-reporting process requires a report if emissions exceed limits, and the other compliance method does not require an exceedance report.

This paper is divided into three sections: (1) what others have done and how their choices fared, (2) what are your choices and what you should do to get in compliance; and (3) what else could have been done (with hindsight).

What Others Have Done and How Their Choices Fared

Research for these articles included lengthy telephone interviews in July - August, 1997. Those interviewed included: six major equipment suppliers, the US EPA, and around a dozen state EPAs or state-based technology transfer organizations. We have also observed actions and results of many users in the past three years.

First of all, through 1996 there has been negligible effect on solvent use except as expected for 1,1,1 TCA.

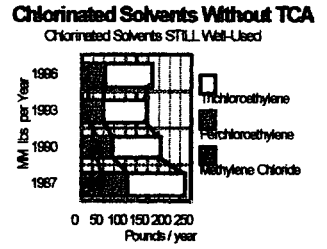
Please see Figures 1 above, and 2 at right[1].

While it may be too soon to see an effect of the NESHAP, plainly little effect has been seen through 1996 — except for methylene chloride, whose use is affected by an additional NESHAP for aerospace operations.

Secondly, the only generalization about US compliance with the chlorinated NESHAP is that it has been controlled by state and local entities.

One state EPA has a list of permitted vapor degreasers that dates from 1972. They anticipate achieving around 85% compliance with the NESHAP.

Figure 2



Another state EPA reports they only received 5 (five) initial notification reports through mid-1997.

Three national firms who produce solvent vapor cleaning equipment report that practically nobody has chosen the idling or total emissions approaches to compliance.

Yet, one regional firm reports that around 80% of their customers for the past 3 - 4 years have chosen among those two compliance options.

One Pollution Prevention group reports that those in their area have converted from cleaning with NESHAP solvents to use of aqueous cleaning technology. They claim to know nothing about those still using solvents on the NESHAP list. In another state, a technology transfer association reports good conversion to the NESHAP because small users could see how it would save them money in solvent costs.

Illinois and Rhode Island appear to have put this situation behind them. Nationally, estimates of overall compliance (including switching to aqueous, no-clean, etc.) range from 25% to more than 50%. A consensus is that at least half of the vapor cleaning machines in the US which are covered by this rule will not have complied with it by the compliance date (seventeen days from NOW December 2, 1997).

Fourthly, the bulk of available data supports the statement that compliance with the NESHAP means compliance with OSHA's exposure limits for workers. Don't turn down serendipity when you find it — EPA and OSHA had little coordination when this NESHAP was developed.

Don't take OSHA limits for granted. You are likely to overexpose your workers to solvent fumes if you were: to implement EPA choice #6 (from Table 6), use MeCl, don't install a working mode cover or practice control of dwell, and locate your machine in a small poorly-ventilated area.

Finally, it is interesting that our responses covered both sides of the question about whether it was large or small firms who had achieved the highest percentage of compliance.

We found user attitudes about this NESHAP varied from ignorance to confusion to various levels of satisfaction. Despite many local and national communication efforts, confusion was the dominant attitude because of the complexity of the rule. Some users were pleased that the NESHAP validated solvent cleaning; others were pleased because the NESHAP would provide them with appropriate motivation to move on to aqueous cleaning. Is this a philosophical view and not a technical or business view?

At some places we found a psychological view — users choosing the engineering controls approach because they could comply with the NESHAP with a purchase order (and lots of record keeping and reporting). These users felt the total emissions method was a gamble, and they had no wish to take a gamble when losing the gamble meant writing an exceedance report to someone who works for Carol Browner (and maybe the local newspaper).

EPA's attempt to provide flexibility appears to have only created confusion, and their insistence on traditional

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1 Data Source: SRI International & Center for Emission Control.

reporting schemes to ensure compliance has created a significant disincentive to the non-traditional compliance methods it offered.

What company wants to select the total emissions limit as its compliance option, if it can't be sure it can meet the limit month to month? More specifically, what plant manager wants to go to his management to tell them that the company has to file an exceedance report with the EPA because production was up last month?

Something else significant has happened regarding the degreasing NESHAP. Much like companies have come to look to the SNAP program to determine what solvents they can use, they appear to look at the degreasing NESHAP to determine how to use them. A number of companies are specifying NESHAP-compliant equipment for use with other solvents. Although they are not required to install NESHAP-level controls, these companies have decided that, for economic, occupational, or environmental reasons, it makes good sense to do so.

What You Should Do to Get in Compliance

DOES THIS APPLY TO ME?
This rule applies to you if you are the owner of a solvent cleaning machine and the solvent in your machine contains more than five weight percent of the 6 solvents listed in the NESHAP[2] . For example, this rule applies to you if you are using a blend of Benzo-Trifluoride with more than five percent Perc (see the MSDS of your cleaning solvent for verification).

Good news is that the rule does not apply if you use small containers with less than 2 gallons volume of the 6 solvents listed in the NESHAP.

Solvents. While that may sound like an narrow subject, there are two - three types of choices of each machine, and a myriad of details about monitoring, record-keeping, training, and reporting about that choice. The result is the EPA's "simplified" guidance document which extends to well over 110 pages!

For this venue, we will limit coverage to only small and large open-top machines. This will amply illustrate the important points about this NESHAP.

The reader is directed to reference 3 for complete coverage[3]: the above in more detail, in-line cleaning machines of various sizes, cold cleaning, enclosed machines, and very large solvent cleaning machines.

VAPOR CLEANING MACHINES (open-top)
There are three options for open machines (vs enclosed). They apply to new or retrofitted, large or small, and batch or in-line units. They are described below, and compared simply in Table 2 and more completely in Table 4.

1. You can buy a new unit or retrofit your existing unit so that your degreaser has **certain engineering controls** which restrict emissions. You are in compliance when you choose among ten combinations of features, and implement one; and your machine meets a few base design requirements. You prove compliance on a continuing basis by monitoring that each engineering feature is performing properly. You must also train your employees and teach them certain work practices.
2. You can prove that your new or retrofitted unit passes a test where it's **emissions are measured when it is idling** (hot, but not cleaning parts), and with the cover on. You can choose any group of engineering controls, though your machine meets a few base design requirements. You prove compliance on a continuing basis by annually measuring the solvent loss when idling. You must also train your employees and teach them certain work practices.
3. You can "simply" **measure your unit's monthly performance**, and compare it to a norm. This choice is

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[2] Methylene chloride (MeCl), perchloroethylene (Perc or perk or perky), trichloroethylene (trike), 1,1,1 Trichloroethane (tri, 1,1,1); and two less common solvents: carbon tetrachloride and chloroform. They aren't used to a significant degree in cleaning operations.

[3] Durkee, J. B., "The NESHAP For Chlorinated Solvents — What You Need to Know and Others Have Learned," *Precision Cleaning*, Vol 5, No. 10, 1997.

also called the "alternate" method. You prove compliance on a continuing basis by monitoring solvent purchase and disposal amounts and reporting a net rolling average consumption vs a norm. There are no requirements about training or work practices.

Note that the method of using engineering controls does not directly controls emissions. It manages the control technologies used to restrict emissions. The idling and total emissions methods are based on measurements of actual emissions. Consequently, the EPA expects higher emissions if the engineering controls method is chosen, because the method of control is only indirect.

	Table 1 — Comparison of Choices for Compliance		
	Engineering Controls	**Idling Emissions**	**Total Emissions**
Pro	Compliance continuously known	Compliance only known after testing, Can be out-sourced,	Compliance only known after billing & calculation, Lowest emissions, Least effect on employees
Con	Most monitoring & reporting burden	Requires tight machine	Requires tight machine

There are three key points about these choices. The first is that they are all acceptable — if you want to use HAPs as cleaning solvents. All three choices have been successfully used by firms throughout the US.

The second key point is that in addition to having to choose among three methods of compliance (engineering controls, idling, or total emissions) with the NESHAP, you have to choose the technologies by which you intend to implement that method. If you choose the engineering controls method, you must choose among the options in Table 4. But, if you choose the idling or total emissions method, you can choose ANY technologies to achieving that compliance.

The third key point with these choices is that compliance achieved with any of them affects only rates of emission, and does not speak to compliance with OSHA's requirements about concentration of HAPs. Specifically, you may be in compliance with EPA regulations and not in compliance with OSHA regulations. Our research for this article suggests that, fortunately, a high percentage of the vapor cleaning machines which meet NESHAP requirements also will meet OSHA requirements.

The engineering controls are described, using the EPA's language, in Table 3. Dwell is the engineering control most difficult to describe. It basically means that the vapor cleaning machine is properly sized for cleaning job it is to do. This means two things: (1) that the open area of the machine is at least 50% bigger than that of the parts in the basket so that solvent is not "pushed" or "pulled" from the liquid or vapor zones as the load is inserted or removed, and (2) the cleaning cycle is long enough to allow the parts to drain off most of the liquid they contain before they are removed.

The cost of achieving proper dwell can be anything. The cost can be a new machine if the existing one isn't large enough -- you'll lose money on increased solvent cost if you retrofit a machine too small for the job. The cost can be nearly zilch if the existing hoist has (or can me modified to have) a programmed stop period where the parts are allowed to drain. Consequently, we have treated the dwell option with a zero cost — which understates it's value.

If you have a batch vapor cleaning machine, and you elect to comply via the method of engineering controls, your choices are listed in Tables 4 (open-top area < 13 SF) and 5 (open-top area > 13 SF). The reason for two tables is that different choices are allowed based on the open-top area of the cleaning machine. This is because the control effect of some choices is better or worse depending on the size of the machine.

For example, choices such as freeboard refrigeration or superheat, which depend upon heat transfer from the freeboard sidewalls, lose their effectiveness the farther the centerline of the vapor degreaser is from the sidewalls. The EPA has specific performance requirements to be certain these two choices are used properly:

- A useful freeboard refrigeration system must produce a cooling at the centerline of the vapor cleaning machine (with the cover closed) so that the temperature at that level is no more than 30% of the solvent's boiling point. See Table 6.
- A useful superheat system must produce a heating at the centerline of the vapor cleaning machine (with the cover closed) so that the temperature at that level is at least 10 °F above the solvent's boiling point. See Table 6.

Recently, top supplier firms have developed some good applications and performance data, for vapor cleaning machines no more than ~ 8 ft on a side. This appears to be the current limit of effect for sidewall-based heat-transfer (cooling or heating) devices.

The choices in Tables 4 and 5 are sorted by our estimates of cost to retrofit an existing machine of "typical" size and condition. The cost information was obtained from various suppliers of equipment, and averaged. The number in the left column is how the EPA identifies each choice so you can simply describe which one you plan to use.

We used the EPA's calculation methods to show how the emission control performance depends upon which engineering controls are chosen. The EPA defines this level of control (generally from 50 to 70%) as Maximum Achievable Control Technology (MACT).

RECOMMENDATIONS

In 1995, we wrote[4] that you should choose the **total emissions** method for compliance.

We still believe that's the right choice, for most firms, because it consumes the least amount of your staff's time in non-productive record-keeping and reporting (please see Tables 2 and 6).

Consequently, if you want to minimize paperwork and meet the needs of the plant manager, the design of the cleaning machine must be one **certain** to meet the requirements of the total emissions method (or idling method).

Let's be specific: we advocate spending a little more capital now to buy a low-emission machine, and more than recover that capital in the future through reduced use of solvent and greatly reduced burden of paperwork.

The opposite is also true. You can choose some of the low efficiency choices in Tables 3 and 4. But you will more than spend those savings on manpower wasted on record keeping / reporting, and increased solvent use.

Our recommended choice for machines **less than 13 SF in open-top area** is: working mode cover; dwell (see discussion in Table 3; freeboard refrigeration, or use superheat if drying is a particular problem; freeboard ratio of 1.25 (adds $800 over 1.0).

This is an excellent choice, because: (1) it will comply with the NESHAP [EPA choice #7 (plus cover) which is the same as EPA choice #3 (plus dwell)], (2) allow use of the simple total emissions method with negligible concern for the plant manager about meeting that limit, (3) reduced solvent use will save money, (4) it is extremely likely to meet the OSHA concentration standards, and (5) it will protect the environment. It is not the choice with the lowest investment, but it is certain to be the choice with the lowest total cost when solvent and labor are included.

Our recommended choice for machines with **more than 13 SF in open-top area** is to choose a firm with successful experience in this situation. They will have learned how to: pack / space / size tubes for maximum heat transfer toward the working zone by convection & radiation means; manage and install large hot oil / high-pressure steam / low-temperature brine heating and cooling systems; avoid hot spots (especially with Perc); avoid disruption of the vapor zone while achieving the desired of level heating or cooling; and stuff this technology / equipment into a small footprint at a cost you can afford.

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[4] Durkee, J. B. Precision Cleaning, Vol 3, (4), page 39 - 48.

What Could Have Been Done *(with hindsight)*

The depth of the requirements in Table 6, compared to the breadth of options in Tables 4 and 5, demonstrate the clearly shows both the "user friendly" and punitive sides to this NESHAP. On one hand, many options were provided. But if you chose the options which produce the most emissions (the engineering controls method), you have the greatest burden of monitoring and record-keeping.

The EPA developed a cunning plan — offer the carrot of simplified monitoring and record-keeping to gain reduced emissions. But, in general, it didn't work.

The vast major of compliant vapor cleaning machines have become so via the engineering control method — the one which produces the most emissions!

The main reason is item 4 in the right-hand column of Table 2: the exceedance report. In general, it has been the "death warrant" for the engineering controls method.

No plant manager wants to file an exceedance report — which could be ultimately forwarded to Carol Browner (EPA Administrator), or their local newspapers (through the Freedom Of Information Act). Few plant managers want to wait until the end of a reporting period to find out if they are in compliance. Most plant managers want to the minimum necessary as soon as possible to get in compliance, and then get on with profit-making issues.

What else could have been done? Two things: (1) make the exceedance report annual, or biannual, while continuing to require monthly monitoring. This should reduce the pressure the plant manager feels; and (2) publicize the existence of successful applications of the total emissions methods. Many believe it can't be done.

Another aspect is complexity. The point to remember is that users demanded flexibility in their public comments to the initial draft of the NESHAP. In this case, we users got for what we wished.

Another approach would have been to combine the above change in reporting of an exceedance, and eliminate all methods but the total emissions method. Users and suppliers would be provided with the EPA's basic data as in Tables 2 through 6 of this paper. This change would cut to the heart of the matter — the EPA wants emissions reduced and under control, users want maximum flexibility and minimum complexity. This change would have been sure to have increased the percentage of users under compliance.

A third aspect is breadth of coverage. Basically, this NESHAP applies to two solvent: Trike and Perc — which are HAPs. It should have been applied to all solvents about which there is some degree of regulation: HAP, VOC, exposure limit less than 100 ppm, That would made it simple for users, effective for regulators, and profitable for manufacturers. In this way, all solvents would have been treated the same. Users would not save money by switching from solvent which is highly regulated because a lot about it's hazards is known to a new solvent about which little is known.

On the other hand, this rule is plainly better than what we might have expected from the EPA of 10 years ago — one method for all, monthly exceedance reports, and quarterly inspections....

Table 2-- General Compliance Options For Vapor Cleaning				
Compliance Method	**You Are in Compliance When**	**You Prove Compliance by**	**Your Records Must Include**	**You Must Report**
Engineering Control Methods	You implement a choice of engineering control methods & train your employees in certain work practices	Monitoring (weekly / monthly) that each control method is properly functioning, and that the practices are being performed	1. Owner's manual and documentation of installation date for lifetime of machine. 2. Monitoring results for 5 years [in paper or electronic form. 3. Basis for calculating machine capacity [only for machines without an air-solvent interface].	1. Initial notification to the EPA that the NESHAP applies to you [at start of construction for new machines, & ***August 29, 1995 for used machines***]. 2. Initial notification to the EPA that you are in compliance with the NESHAP. 3. An annual compliance report based on your monitoring and record keeping. 4. ***An exceedance report [when you exceed NESHAP limits***].
Idling	Measured emissions when idling are below a specified value, & you train your employees in certain work practices	Monitoring (yearly) that emissions when idling are below a specified value, and (monthly) that the practices are being performed		
	<u>Batch</u> ◆ 0.045 lb / hr -SF solvent-air interface area <u>In-line</u> ◆ 0.021 lb / hr -SF solvent-air interface area			
Total Emissions ("Alternate")	3-month rolling average of monthly **NET** use of solvent (including waste recovery) is below a specified value	Monitoring (monthly) your solvent purchase and disposal invoices, and compare 3-month **NET** rolling average to a specified value		
	<u>Batch</u> ◆ 30.7 lb /month -SF solvent-air interface area <u>Existing In-line</u> ◆ 31.4 lb /month -SF solvent-air interface area <u>New In-line</u> ◆ 20 lb /month -SF solvent-air interface area <u>Without Air-Solvent Interface</u> ◆ 85 lb /month $\times(\text{Vol})^{0.6}$			

Table 3– Description of Emission Control Methods For Vapor Cleaning			
Emission Control Method	**EPA Description**	**Cost < 13 SF /> 13 SF**	**Control Efficiency**
Working Mode Cover	Cover means a lid, top, or portal cover for a solvent cleaning machine. Working mode means the time period when the solvent cleaning machine is turned on and is actively cleaning parts.	6,000 / 10.000	40%
Freeboard Ratio = 1.0	Freeboard height means for a batch cleaning machine the distance from the solvent/air interface to the top of the cleaning machine. For an in-line cleaning machine, it is the distance from the solvent/air interface to the bottom of the entrance or exit opening, whichever is lower. Freeboard ratio means a ratio of the solvent cleaning machine freeboard height to the smaller interior dimension (length, width, or diameter) of the solvent cleaning machine.	1,000 / 3,000	20%
Superheated Vapor	Superheated vapor means employing the use of heating coils that boil liquid solvent generating solvent vapors that are heated to temperatures that are more than 1.5 times greater than the solvent boiling point.	7,000 / 11,000	50%
Reduced Room Draft	Reduced room draft means decreasing the flow or movement of air across the solvent cleaning machine to meet the specifications of 50 ft / min.	1,000 / 1,000	40%
Dwell	Dwell means the technique of holding parts within the freeboard area but above the vapor zone of the solvent cleaning machine. Dwell occurs after cleaning to allow solvent to drain from the parts or parts baskets back into the solvent cleaning machine. Dwell time means the required minimum length of time that a part must dwell, as determined by § 63.465(d). Proper dwell time decreases emissions by ensuring that the parts have reached the solvent temperature prior to removal from the machine (if parts have not reached the solvent vapor temperature, condensation would still occur as parts are withdrawn from the machine and solvent carry-out losses would increase). This time is no less than 35% of the time required for the parts or basket to stop dripping when immersed at room temperature.	$0	30%
Freeboard Refrigeration	Freeboard refrigeration device (also called a chiller) means a set of secondary coils mounted in the freeboard area which carry a refrigerant to provide a chilled air blanket above the solvent vapor.	11,000 / 30,000	40%
Carbon Adsorber	Carbon adsorber means a bed of activated carbon into which an air-solvent gas-vapor stream is routed and which adsorbs the solvent on the carbon.	30,000 /100,000	60%

Table 4-- Control Combinations for Batch Vapor Cleaning Machines < 13 SF			
EPA #	Control Combinations	Estimated Control Efficiency	Estimated Price
8	Freeboard Ratio of 1.0; Reduced Room Draft; Dwell	69%	$2,000
4	Freeboard Ratio of 1.0; Superheated Vapor; Reduced Room Draft	78%	$9,000
1	Working Mode Cover; Freeboard Ratio of 1.0; Superheated Vapor	73%	$14,000
7	Freeboard Refrigeration Device Dwell	58%	$11,000
5	Freeboard Refrigeration Device Reduced Room Draft	70%	$12,000
6	Freeboard Ratio of 1.0 Freeboard Refrigeration Device	46%	$12,000
3	Working Mode Cover Freeboard Refrigeration Device	64%	$17,000
2	Superheated Vapor Freeboard Refrigeration Device	70%	$18,000
10	Freeboard Ratio of 1.0; Superheated Vapor; Carbon Adsorber	82%	$38,000
9	Freeboard Refrigeration Device Carbon Adsorber	76%	$41,000

The base design requirements which MUST be included with ANY of these equipment compliance options are: (1) a cover which is closed except when parts are being cleaned, (2) a freeboard ratio > 0.75, (3) some "automated" parts handling system with which it is impossible to move the work more than 11 ft /sec, (4) liquid and vapor level indicators with safety shut-offs, (5) a primary condenser, and (6) a carbon adsorption unit if a lip exhaust is used to reduce exposure of workers to solvent.

Table 5-- Control Combinations for Batch Vapor Cleaning Machines > 13 SF			
EPA #	Control Combinations	Estimated Control Efficiency	Estimated Price
4	Freeboard Ratio of 1.0; Superheated Vapor; Reduced Room Draft	78%	$15,000
2	Freeboard Refrigeration Device; Reduced Room Draft; Dwell	79%	$31,000
6	Freeboard Ratio of 1.0; Freeboard Refrigeration Device; Reduced Room Draft	73%	$34,000
5	Superheated Vapor; Freeboard Refrigeration Device; Reduced Room Draft	85%	$42,000
1	Freeboard Ratio of 1.0; Superheated Vapor; Freeboard Refrigeration Device	73%	$44,000
3	Working Mode Cover; Superheated Vapor Freeboard Refrigeration Device	82%	$51,000
7	Superheated Vapor; Freeboard Refrigeration Device; Carbon Adsorber	88%	$141,000

The base design requirements which MUST be included with ANY of these equipment compliance options are: (1) a cover which is closed except when parts are being cleaned, (2) a freeboard ratio > 0.75, (3) some "automated" parts handling system with which it is impossible to move the work more than 11 ft /sec, (4) liquid and vapor level indicators with safety shut-offs, (5) a primary condenser, and (6) a carbon adsorption unit if a lip exhaust is used to reduce exposure of workers to solvent.

Table 6 — Requirements for Control Devices Used in Vapor Cleaning Machines				
Control Device	**Compliance Requirements**	**Record-Keeping Requirements**	**Violations of NESHAP**	
			Immediate	**If Not Corrected in 15 days**
Working Mode Cover	**Monthly** you must ◆ Inspect cover ◆ Note cover closed when working	◆ Cover condition and it's closure ◆ Must be closed when working ◆ Open only when parts added & removed	--	Cracks, holes, or other defects
Freeboard Ratio = 1.0	Manufacturer's certification of ratio	◆ Freeboard Height ◆ Smallest interior freeboard width	< 1.0	
Superheated Vapor	Check temperature **weekly** at ℄ inside superheated vapor zone while machine is idling	Minimum values: MeCl 114 °F TCA 175 °F TCE 199 °F Perc 260°F	Superheated vapor zone is not determined and maintained	Solvent vapor at center of the superheated vapor is not above the given values
Reduced Room Draft (in room or enclosure)	◆ Air velocity in room or enclosure with machine must be < 50 ft / min ◆ Establish during initial test of machine ◆ Must be reset **immediately** if conditions change	◆ **Quarterly** measure air velocity in room; **Weekly** monitor conditions in room. ◆ **Monthly** measure air velocity in enclosure; inspect conditions within enclosure	Readjust parameters under which the reduced room draft is achieved	If air velocity in room or enclosure with machine is not < 50 ft / min.
Dwell	◆ Measure time parts are held above vapor zone ◆ Time determined based on full drainage of liquid from parts ◆ Set at machine installation, or when parts change	**Monthly** check that dwell (hold) time is >35 % of that for full drainage of liquid from parts	Determine and maintain	
Freeboard Refrigeration	Check temperature **weekly** at ℄ above vapor zone while machine is idling	Limits are: MeCl 31 °F TCA 50 °F TCE 51 °F Perc 75 °F	--	Values are exceeded
Carbon Adsorber	◆ Concentration < 100 ppm ◆ Can't be bypassed during desorption ◆ Located above cover	Weekly measured values of exhaust concentration	--	Exhaust concentration of covered solvent exceeds 100 ppm

Policy: Technology Transfer

By: Eng. Salwa El-Tayeb
Ozone Unit Coordinator

Background:

The Government of Egypt is one of the initial signatories of the Vienna Convention and the Montreal Protocol (MP) which were ratified by Egypt started as early as 1988. Egypt actively participated in all international meetings dealing with the protection of the stratospheric ozone layer. The Egyptian Government has shown sustained commitment to reduce the consumption of Ozone Depleting Substances (ODS). Activities to protect the ozone layer started as early as 1986, since then, it has moved aggressively to reduce ODSs consumption. A reduction of more than 60 % in demand for ODSs was achieved in 1991, primarily through a government ban on the use of CFCs in aerosols.

According to Egypt's country programme, the total ODS consumption was 2890 Tons weighted as an ODP of 3376 [reference year 1990.

Although Egypt qualifies for a ten year delay in the phase-out of ODSs, completion will be achieved by the end of 1999, i.e. 11 years ahead of the deadline.

Operational Structure:

1.1 **The Egyptian Environmental Affairs Agency** (EEAA), which is directly affiliated to the Cabinet of Ministers, is the competent authority for the implementation of all international environmental agreements and all their related protocols. For optimal management of the implementation of ODS phase-out, an **Ozone Layer Protection Unit** (OLPU) was established within the Technical Office of EEAA. This acts as the national focal point for all matters related to Ozone Layer Protection. This is supported by an **Ozone Panel** acting as an advisory body that recommends actions and measures necessary for phase-out accomplishment. The panel is made up of all government units involved in the phase-out programme.

An Ozone Layer Protection Unit (OLPU) was established as an institutional strengthening project within the EEAA in 1993 funded by the MLF for the amount of US$ 263,450 and implemented by UNIDO. The OLPU is assisted by technical consultants who are available on a regular basis, for expert advice.

A National Ozone Panel was created in cooperation with the Egyptian Federation of Industries (EFI) to play a consultative role in the formulation and promulgation of specific national ozone policies.

Phase-out Strategies and Achievements:

The phase-out strategies, target reductions and schedules and technology choices for the different sectors using ODSs is described in the following sections.

However **in the Aerosol Sector,** the Government of Egypt has an active and an on-going commitment to phasing out ODS use. A reduction of more than 60% in demand for ODSs has been achieved primarily through a Ministerial decree No. 977 issued in 1989 banning the use of the chlorofluorocarbons (CFCs) in the new aerosols industries starting 1990 and the ODS Phase-Out Programme has already started before the formulation of the Ozone Unit In addition 90% of the enterprises switched to the new technology which is Butane and LPG on their own initiative and the rest 10% is used by the cosmetics and medical enterprises.

ODS Phase-out for the Foam Sector

1. The Phase-out Strategy

The CFC consumption in 1991 in the Egyptian foam sector (excluding foams for domestic and commercial refrigerators and freezers) was assessed as 722 tons (Egypt Country program). At that time, the government identified thirty two (32) foam manufacturers that utilized CFCs in their production process. Table 1 lists the ODS consumption per category, as estimated at the time. Five more companies were identified later which consumed 202 tons annually. Therefore the total annual ODS consumption in the foam sector was actually 939 tons in 1991.

Category	ODS mt		Total
	CFC-11	CFC-12	
Flexible PUF, Slabstock	229		229
Flexible PUF, Molded	46		46
Integral Skin and RIM PUF	25		25
Rigid PUF, Panels	25	6	31
Rigid PUF, Miscellaneous Applications	104		104
Extruded Polystyrene Foam Sheet	43	135	178
Extruded Polystyrene Foam Board		140	140
Total	**456**	**281**	**737**

Table (1): Status of ODS phaseout efforts based on the 1991 Consumption

In June 1993, an ODS phaseout plan for the foam sector was submitted to the Executive Committee (ExCom) of the MLF. The plan foresaw the preparation of segment specific multi-plant phaseout during 1994, beginning with flexible foams. Implementation during 1994/1995 would accomplish complete phaseout in 1996, and so will thus be in line with the schedule for developed countries.

In 1996, OLPU supported by the UNDP updated the ODS inventory and phaseout strategy for the sector. The transition to ODS substitutes is accomplished at a rate consistent with the availability of technology and to be fully accomplished over the period 1992 -1998.

The overall annual growth rate in the sector is still estimated at about 20% with below average growth in flexible slabstock and extruded polystyrene sheet. Unconstrained growth would lead to an estimated ODS consumption of 2,338 tons in 1996, in the year 2000 (Table 2).

SCENARIO	91	92	93	94	95	96	97	98	99	2000
Unconstrained Growth	939	1127	1353	1623	1948	2338	2805	3366	4039	4847
Target	722	850	900	750	600	450	300	150	0	-
Forecast	939	1127	1215	1166	896	445	215	0	-	-

Table 2: ODS Consumption Scenario's in the Foam Sector

The completion of the strategy will make Egypt one of the first Article 5 countries -perhaps the first one to achieve total phaseout of the use of CFCs in the foam sector. This could serve as a learning example for other countries with similar conditions.

2. Description of the Sector:

Production of foam in Egypt can be classified on the basis of composition, chemical and physical characteristics, manufacturing process and application.

3. Technology:

The following general criteria of technology selection were applied in Egypt:
- Proven technology.
- Commercially available.
- Acceptable processing.
- Safety considerations.
- Environmentally acceptable.
- Economically viable.

A- Non- insulating foam:

1. Thermoplastic foam (Extruded Polystyrene/ Extruded Polyethylene):
Alternative technology:

There are several options to replace CFC-12 in the production of extruded polystyrene/ polyethylene, such as:
- Nitrogen gas.
- Carbon dioxide gas.
- Hydrocarbons (N-pentane, isopentane, butane)
- The "berstroff" technology.
- HCFC-22
- HFC-134A
- HFC-152A
- HCFC-142B
- Liquid petroleum gases (Butane)

Technology Selected:
Butane was selected as an economic attractive alternative, if applied with the necessary safety precautions to mitigate the risks, originating from the high flammability of the substance, and will perform well both for polystyrene as well as for polyethylene.

2. Flexible PUF (Slabstock):
Alternative technology:
- Methylene Chloride.
- Hyper cure technology.
- Hydrocarbon.

Technology Selected:
Replacement of CFC-11 with Methylene Chloride. In addition, precautions to eliminate the adverse effects of Methylene Chloride were applied mainly with proper ventilation, safety measures for worker protection and limiting the emissions to acceptable levels.

3. Flexible PUF (Molded):
Alternative technology:
- Polyol systems that allow the elimination of an auxiliary blowing agent are currently available while maintaining desired properties. In addition, the chemicals and the molds have to be conditioned (heated).
- Water blown system

Technology Selected:

The standard replacement for CFCs is an all water blown system.

4. Integral Skin PUF (Semi-rigid ISF):
Alternative technology:

There are several options to replace CFCs in the production of integral skin PUF, such as:
- HCFC-141b
- HCFC-22, HFC-134a, 152a
- Pentane
- Water blown foams

In addition, compounds such as Methylene chloride have been suggested, but these are restricted in applicability.

Technology Selected:

A combination of reduced HCFC and a water based technology has been selected for the Egyptian automotive and furniture industry.

B- Insulating foam:
Alternative technology:

There are currently three main directions in the development of CFC-free systems for thermoses insulation foams:
- Partial water/ HCFC-141b>
- Partial water/ HCFC-22, 142b>HFC-134a, 152a
- Pentane

In addition, compounds such as perfluoroalkanes, HCFC 123, fluorinated ethers and 2-chloropropane have been suggested, but are immature in technology, of limited availability or toxicologically suspect.

Technology Selected:

Pentane as an alternative blowing agent has currently been introduced commercially. Its flammable character requires adequate safety measures.

The Current Status:

Substantial progress was achieved in three years and the rate of phase-out is well within the targets. There were, however, impediments worth highlighting:
- Several projects for extruded polystyrene foam were not approved based on potential incremental operating benefits to an amount that would force the recipient in very substantial co-financing. The enterprises could not provide this.
- Umbrella projects for molded flexible and integral skin foam manufactures were deferred pending the formulation and acceptance of a global strategy for small ODS users.

This would require substantial financing by the recipient which in all cases was beyond the enterprise means.

ODS Phase-out for the Refrigeration Sector

1. The Phase-out Strategy:

Phase-out of ODS based gases in the refrigeration industry in Egypt in was carried out in two stages:
I) Phase-out of CFC refrigerants between Jan. 1, 1994 and 1998
II) Phase-out of CFC foaming agents over the period 1996 to Jan. 1, 1999

Economic and developmental implications of the proposed strategy. OLPU - EEAA undertook detailed analysis of this issue:

At the micro level, this entailed an estimation of the incremental costs associated with the testing, development and installation of new non-ODS technologies and of the firms' competitive position in international markets. Since there is a notable over capacity in the domestic refrigeration sub sector which cannot be absorbed by domestic demand, the export potential of Egyptian non CFC based products must be explored and exploited, regardless of individual action by the enterprises.

At the macro level, the analysis focused on: the developmental effects in terms of employment and wealth; backward and forward linkages with related industries, notably air conditioning, cold storage, and cold transport systems, as well as with the professed targets of food security, preservation of "seasonal crop" and other related export-oriented food industries.

The above analysis enables the EEAA through the Ozone Panel to develop a parallel action plan for phasing out CFCs in the air conditioning sector and to implement the phasing out of ODSs in a systematic manner without necessarily jeopardizing the developmental objectives of the concerned industrial sectors.

Policy measures:

The EEAA (OLPU) in collaboration with the National Ozone Panel has elaborated a long term plan which establishes a consensus for activities in institutionalizing the National Ozone Policy predicated on a prompt phase-out of ODS consumption.

The following measures are achieved:
- Elaboration of manufacturing standards for new technologies, including safety regulations for hydrocarbons.
- Introduction of ODP safe maintenance practices in existing refrigeration equipment (especially to collect and recycle CFC-12 based insulation equipment by 1996.
- Ban the imports of CFCs based equipment starting from 1995.

The following measures are to be achieved during 1997:
- Abolish the import taxes on equipment needed for the conversion of refrigerator manufacturing plants to non CFCs based refrigerators.
- Ban the use of CFCs in new refrigerators and air-conditioning starting from 1998.
- Ban the imports of CFC-12 for refrigerator manufacture by 1997.
- Ban imports of all CFCs in refrigeration and air-conditioning by 1999.
- Financial incentives for collecting and scrapping of old CFC based refrigerators.
- Higher import duties on CFC chemicals and other CFCs to induce users to switch to non CFC equipment.
- Some CFCs will be imported and used for many years to come. Since much of the existing stock cannot be retrofitted economically. A licensing/ quota system for ODS users should be established to maintain the unconvertible units as long as it is technically and economically feasible to do so.

2. Description of the Sector:

A) Domestic Refrigeration Sub-sector:

The subsector for domestic refrigerators and freezers in Egypt consists of 9 manufacturers of which four companies are responsible for over 80 percent of the ODS consumption of CFC11 and CFC12.

The total installed production capacity for refrigerators and freezers is about 1,000,000 units per year, but the present production is only about 50%. The manufacturers expect an increase of about 10 percent per year.

In total about 7,000,000 refrigerators and freezers are in use in Egypt of which about 10 percent per year will be serviced and a part of them recharged during refrigeration service with CFC12. Service staff very often use CFC12 for washing/ flushing of the cooling systems, instead of using vacuum pumps and charging boards. This causes up to 200 percent excess CFC12 consumption in the service sector.

B) Industrial and Commercial Refrigeration Sub-sector:

It consists of 11 manufacturers, 5 for the industrial walk-in cold rooms, cold stores, freezers and air-conditioning, 6 manufacturer for commercial refrigerators, freezers, ice-makers and display cases, cabinets ...etc.

In 1991 CFC consumption in the CP, including that used in insulation foam in the domestic, industrial and commercial refrigeration sectors, was 1,045 tons.

With a forecast growth rate of 5% per annum, this would lead to consumption of 1,2010 tons in 1994, and 1,620 tons in 2000.

According to strategy for this sector, targeting annual ODS consumption reductions beginning 1996 and elimination of ODS consumption in the manufacture of new commercial refrigeration equipment by the end of 1997.

1- Refrigerant:

Alternative technology:

None of the known substitute refrigerants can be looked upon as an ideal "drop-in" solution. This means that in order to use the refrigerants, the compressor, its lubrication, evaporator, tubing, and many other details must be checked and modified, when required.

Technology Selected:

HFC-134a is the most promising replacement. The present trend is to use R-134a as refrigerant. The equipment suppliers to the Egyptian market have indicated that they will begin to supply compressors using 134a during 1994. Those companies involved in assembly and service of that equipment will need reclaim/ recycle equipment for the new units as well as for the existing R-12 and R-502 refrigerants. Technicians will have to be trained on the proper use of the servicing equipment.

2- Insulation Foam (CFC-11 substitutes):

Technology Selected:

Cyclopentane is being used commercially in Europe. Its flammable character requires safety considerations and limits its use to factories that can be adapted to meet those requirements. Due to the requirement for the best insulation properties in cold storage applications, cyclopentane would be the best choice for these applications. From a safety standpoint, the factories will require some ventilation improvement and possible replacement of some electrical equipment in the foaming areas.

The Current Status:

Although substantial progress was achieved in the almost three years and the rate is well within the targets that are developed from the strategy as mentioned in the Country program, there were also drawbacks to register:

- Domestic refrigeration sector: 4 projects (9 production enterprises) are under implementation and expected to be completed before the end of 1997.

- Commercial and industrial refrigeration sector:

  - 2 projects are completed (MCMC and Koldair Cos.).
  - 4 projects (9 production enterprises) are under implementation and expected to be completed during the first quarter of 1997.
  - 1 project (2 production enterprises) is submitted for fund approval.

- Servicing activity including recovery, recycling, reclaiming and training is considered a remaining activity to be included in the OLPU Work Programme for 1997.

Servicing of existing equipment using CFCs:

The introduction of more efficient servicing techniques including recovery, recycling and reclamation for the existing equipment aims at effectively reducing CFCs consumption and emissions and assisting the refrigeration manufacturers as focal points in providing assistance and training for others who serve the refrigeration and air conditioning including the mobile air conditioning (MAC) equipment.

ODS Phase-out for the Solvents Sector

1. The Phase-out Strategy:

The solvents sector is estimated to account for 5.6 % of Egypt's total consumption of ODSs in 1991. ODS consumption in the solvents industry is split among electronics, optics, metal cleaning and other processes. Cleaning processes used in the electronics, optics, and metal industries consumed per year, using about 36.4 mt of CFC-113, 200 mt of MCF and 51.9 mt of CTC. The problem in Egypt is that there are many small and diverse uses for ODS solvents. However, the total use is small. The forecast assumes that there will be a gradual transition to other solvents as prices rise and supplies of ODS solvents diminish. Assistance is acutely required to set up a series of awareness activities dealing with the phasing-out of ODS solvents for the small-scale users.

Process Type	No. of Enterprises	MT/ Year		
		1,1,1 Trichloro ethane	CFC113	Carbon Tetra-Chloride*
Electronic cleaning process	4	10	16	15
Metallic cleaning process	6	137	---	5
Optics glass cleaning process	2	5	4	10
Polyurethane products cleaning process	2	140	---	---
Others	---	---	---	120

*Laboratory Use and Direct Cleaning Processes

Alternative technology:

The aqueous and semi-aqueous cleaning, and cleaning with petroleum solvents, ketones, and alcohols are to be viewed as acceptable for new alternative technologies to phase-out the utilization of ODSs in cleaning processes. Petroleum solvents, alcohols, and ketones are presently used in some sectors of manufacturing and repair industries for cold cleaning applications. Petroleum solvents (mineral spirits, kerosene, stoddard solvent) show good solvency for most contaminants. Alcohols (e.g. ethanol, isopropanol, and glycol ethers), have been used in certain applications requiring effective solvent power for defluxing operations in engineering industry. These solvents, however have several limitation. their flammability restricts their use in enclosed systems and in vapor degreasing operations. The common alcohols and ketones have flash points that are quite low and are considered flammable. Also, alcohols as well as ketones are not compatible with many polymeric and elastomeric materials. In addition, these solvents are photochemically reactive.

Technology Selected:

Examples of alternative technologies introduced are:
Siltal Co.: A batch operation immersion type ultrasonic cleaning machine with a programmable transport system controlled by a microprocessor-based system.
Technopol: A batch operation aqueous cleaning machine with a microprocessor- based control system.
Arab International Optronics: Four batch operation immersion type ultrasonic cleaning machine controlled by a microprocessor-based system.
Abbasol: A batch operation cleaning machine with a microprocessor-based control system.
Three Electronics Companies: introduced a new type of mixed hydrocarbon (A3-products) processes: fully automatic cleaning/spraying, vapor rinsing with vacuum drying for flux removal from electronic assemblies, and immersion cleaning with Ultrasonics, vapor rinsing with vacuum drying for cleaning of metal parts.

ODS Phase-out for the Halon Sector

The total annual consumption of halons given in the country programme are 15 tonnes halon 1211 and 30 tonnes halon 1301 respectively, imported mainly from India and china.

The Phase-out Strategy:

The overall approach is to promote the use of non-halon fire protection technology, limit safety impact and phaseout cost by developing national capacity, and implement halon management and banking programme.

The specific objectives of the project are to:

- Ensure that sufficient halon is recovered to cover demand for existing uses during the phaseout.
- Plan and monitor a halon banking programme.
- Prevent unnecessary emissions of halons
- Provide technical assistance to users of halons.
- Carry out training and education programmes on fire protection without using halons and facilitate transfer of alternative technology.
- Participate in a regional network of halon bank. (Indonesia, Malaysia, Philippines, Brunei, Singapore and Thailand).

Alternatives like FM 200, NAF S3, CEA 410, Inergen and Water mist, which have been introduced in the market, are not use by the existing fire equipment companies. They do not have the technical training to design and install such systems, nor do they have the legal licensing agreement to import and sell new alternatives.

The country programme is based on the strategy and action for the phaseout of the use of halons in Indonesia:

- Setting of an Advisory halon Phaseout committee, consisting of the fire Protection Industry, Users of halon and Ministries and Departments with the aim to monitor the implementation of the phaseout programme.
- Regulating import of newly produced halons through a case by case approvals.

Alternative Technology:

An Inergen, water mist and FM 200 fire extinguishing system will be installed in a fire test room to be used for education and training programmes. Access to alternative fire extinguishing systems is required both for demonstration and education and training purpose, it will be most cost effective to establish a test room at the Civil Defense Organisation and install the various types of systems and use them for demonstration and education purpose at the same time. Effort will be made to obtain alternative fire extinguishing systems free of charge from the suppliers. The project budget however cover both the cost of test/ training/ demonstration room and alternative fire systems.

Technology Selected:

This project is based on the recommendation on halon management provided in the Halon Technical Option Report and by UNEP information on halon management. it is also based on information, and experience on halon banks operating in Australia, Canada, Denmark, Malaysia, Switzerland, United Kingdom, Holland, France and USA.

The Current Status:

UNDP completed the strategy and project documents were completed with technical assistance from UNDP. They will be submitted to the ExCom for approval.

Methyl Bromide

Completed preparing of Methyl Bromide alternatives project for soil fumigation and silos and stored products to prepare the demonstration project so as to be funded either through the Bilateral cooperation or the ExCom rules.

Year	Quantity of MB imported for use in country (Kilograms in 1994)	Estimated quantity used in country (Kilograms in 1994)
1994	572,100	
1993	531,182	
1992	272,000	approximately all
1991	301,000	
1990	213,920	

Summary of surveys results: estimates of the quantity of Methyl Bromide imported and used nationally.

Area of application	Estimated quantity of MB used in 1994 (Kilograms)
Soil treatment	
Quarantine treatments i.e. treatments to meet official standards of quarantine authorities.	170,063
Post-harvest treatments excluding quarantine, e.g. stored grains	227,037 (silos and stored products)
Other miscellaneous treatments e.g. buildings, transport, termite mounds	175,000 (soil fumigation)
Total	

Methyl Bromide used for soil, quarantine and other applications in 1994.

According to the recommendations of the Ozone Panel, the Ministry of Agriculture and Land Reclamation states some regulations to optimize the use of Methyl Bromide for silos and stored products fumigation.

For soil fumigation, Governmental and some of the private sector combine biological and Methyl Bromide for treatment of soils starting from 1996.

1997
A Critical Year for ODC Elimination in Army Facilities

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Introduction

In response to the London Amendments to the Montreal Protocol and the Clean Air Act Amendments of 1990, Congress inserted language into the Defense Authorization Act for Fiscal Year 1993 addressing ozone-depleting chemicals (ODCs). Section 325 of this Act created the Department of Defense (DoD) Ozone Depleting Substance (ODS) Reserve, managed by the Defense Logistics Agency. Section 326 prohibited any DoD activity from letting a contract requiring the use of an ODC, without a certification of need and approval by a senior acquisition official.

In 1994, domestic production of halon ceased. Also in 1994, the Army issued policy directing the development of installation ODC elimination plans. In 1995, the Army issued the Strategic Guidance & Planning for Eliminating Ozone-Depleting Substances from U.S. Army Applications, a comprehensive policy and planning document, which included detailed instructions on how to establish and execute these ODC plans.

In 1996, domestic production of chlorofluorocarbons (CFCs) ceased. The Army issued policy stating installation Commanders are responsible for ODC elimination at their facilities, and that installations would be free of class I ODCs by October 1, 2003.

Two months ago, at the Ninth Meeting of the Parties and Tenth Anniversary of the Montreal Protocol, thousands of dignitaries, bureaucrats, and activists gathered to acclaim their mutual efforts in impeding the destruction of the ozone layer. Though there were a few minor amendments enacted amongst admonitions to "stay the course," for the most part the attendees declared victory and eagerly redirected their sights toward the threat of global climate change rising ominously on the horizon.

So ... where's the problem? Haven't we won the war? The ozone layer is recovering, laws and regulations are in place, alternative technologies are available, and the country and the world are moving forward. It's all over and done with, right?

Wrong! Eighty percent of the Army building chillers that used CFC refrigerants in 1992 are still around and are still using CFC refrigerants. That's close to 1,000,000 pounds of installed CFCs. Ninety percent of the halon 1301 fixed fire suppression systems installed in Army buildings in 1992 are still installed in Army buildings in 1997. That's over 800,000 pounds of halon. And some Army industrial operations are still dependent on methyl chloroform, even though it went out of production two years ago!

So the problem, in a nutshell, is implementation. There's great policy and guidance for ODC elimination in Army facilities. But there's also a serious disconnect between that policy and the actual replacement of ODC equipment at the installation level.

R-12 Availability

Three issues that surfaced over the winter and spring of 1997 impressed upon the Army the seriousness of the ODC situation. First, the Army conducted an analysis of recently released government and industry data on R-12 availability which revealed a strong possibility of area or regional spot-shortages at the end of the summer. Over 70 million pounds of R-12 were used by the automobile industry over the summer of 1996, and less than 60 million pounds were projected to be available for the summer of 1997. This included 7 million pounds recovered from building chillers last year.

In the spring of this year, the most recent Army data identified over 200 R-12 building chillers operating on Army installations. The Army also has close to 50,000 R-12 cold storage units and warehouse refrigeration systems still in use. All told, there were over half a million pounds of R-12 installed in Army facilities equipment. And over 90% of this R-12 is maintained and serviced through commercial contracts.

Therefore, unless an installation has a good recovery and recycle program in place and provide R-12 to their service contractor as government furnished equipment (GFE), the service contractors will have increasing difficulty in buying the R-12 they need to service Army equipment. This in fact has occurred, although no installation has reported (yet) that their contractor was unable to eventually find a source for the refrigerant.

Understandably, the price of R-12 continues to escalate, reaching almost $50 per pound by the end of August. Even at that price, most distributors claim that the price has been significantly **depressed** due to the flood of illegal imports. Tightened controls on the black market may push the price of R-12 to as much as $100 per pound by the middle of next summer -- if it's available at all.

TCA Availability

The second ODC issue that surfaced early in 1997 was the continued use of methyl chloroform in some Army industrial operations, and concern over the continued availability of this CFC solvent to support those operations.

Existing alternative technologies have been identified. Designs have been completed. The Army is prepared to retrofit every remaining industrial use of TCA. However, the question is funding. The Army has no central funding to support this change-over. All capital improvements to Army industrial operations must funded by their associated military customers, either directly or through overhead, in a similar fashion to their civilian counterparts (and competitors).

In practice, however, Army industrial management doesn't have the same flexibility with capital investments as the commercial community does. In many instances, the Army plant must wait until the product or service demand is formally identified and established before they can proceed with process improvements. When a solvent conversion can take nine months or more to complete, this restriction becomes a nightmare. In some instances the new ODC-free technology can be installed in parallel to the existing production line, thus minimizing disruption to the current product flow. But funding (and timing) still remain significant problems to industrial ODC conversions.

EPR Guidance

The third issue that surfaced early in 1997 was associated with a major revision to the guidance for the Army's Environmental Program Requirements (EPR) reporting system. The EPR is the Army's evolution of the old Office of Management and Budget (OMB) A-106 reporting system. Army installations use the EPR to report environmental projects to Major Command (MACOM) headquarters and headquarters Department of the Army (HQDA) staff.

The EPR is how each Army installation justifies its environmental budget. Specific guidance is provided by HQDA on how a project should be categorized and rated, with compliance projects (those driven by laws and/or subject to fines) given the highest priority. Priority directly equates to probability of funding.

There's no law saying ODCs can't be used or ODC equipment has to be replaced. So ODC elimination is by definition not a compliance issue. Since they aren't considered compliance projects, ODC elimination projects don't have, nor have ever had, a high priority. And even though Army policy has for years identified ODC elimination as a readiness issue, and not an environmental issue ... no central funding is available.

Therefore, any funding for ODC equipment replacement has to come through the installations' real property maintenance account (RPMA). The RPMA is part of the installation's day-to-day operating fund, and has to compete for funds with the electric bill, water bill, salaries, and the like. RPMA can be used to replace equipment at the end of it's useful life -- but an R-12 chiller installed in 1985 could easily last 30 years, or 12 years past the Army deadline of October 1, 2003.

The draft EPA guidance circulated for comment in the spring stated nothing new about ODC elimination, and directed nothing different than how things were already being done. It did, however, officially highlight the disconnect between the standing policy on ODC equipment elimination and the installations' ability to actually execute that problem.

ACSIM Program Review

Therefore, in April of this year the Army ODC Elimination Program requested HQDA to conduct a review of the program, for the purpose of eliminating the disconnect between policy and execution. The first outcome of this review was a restatement of the existing Army policy for ODC elimination in facilities. It was released in an Assistant Chief of Staff for Installation Management (ACSIM) memorandum on July 3, 1997, and was presented as follows:

1. **Installation Commanders Are Responsible for ODC Elimination**
   - -- Responsible for the documentation of all installation ODC elimination requirements using the Environmental Program Requirements (EPR) report.
   - -- Responsible for preparing and maintaining an inventory of installation-owned and tenant-owned ODC equipment installed in their installation facilities.
   - -- Responsible for the development and execution of installation ODC plans.

2. **Tenant Commanders Are Responsible for Complying with Host ODC Policies and Supporting Host ODC Elimination Efforts.**

3. **Class I ODCs Must Be Eliminated from All Facilities on Army Installations by the End of FY03.**
   - -- Class I ODCs are defined by Section 602(a) of the Clean Air Act of 1990.

4. **Installations May Not Contract for the Use of Class I ODCs.**
   - -- Public Law 102-484, Section 326, prohibits the Army from letting contracts that require the use of Class I ODCs. This includes contracts for the servicing of AC&R equipment and fixed fire suppression systems, as well as the direct purchase of CFC refrigerants and halon.
   - -- Approvals may be granted only through the preparation of a technical certification of need identifying that no ODC alternative is available, and the formal approval of a General Officer or Senior Executive Service member.

5. **All Class I ODCs Installed in Army Facilities Must Be Recovered.**
   - ODCs must not be sold, traded, turned in to the post Defense Reutilization and Marketing Office (DRMO), or otherwise transferred from Army ownership. All ODCs in non-sealed systems must be recovered when the system is retired.
   - Halon installed in fixed, total flooding fire suppression systems must be turned in to the Army ODC Reserve when the system is retired. This halon must not be reused to support another facility fire protection system on the installation.
   - Recovered CFC refrigerants may be reused to support another CFC systems on the same installation. This is referred to as "cascading" and is recommended in lieu of purchasing CFC refrigerant to service existing equipment.

6. **ODC Alternatives Must Be First Approved by the EPA Significant New Alternatives Program and Receive a Toxicology Clearance from the Army Surgeon General Before Use in Army Facilities.**

Also included in the ACSIM memorandum was a comprehensive data call, to identify exactly what ODC equipment remained and at what installations. This information, received last month, is currently being compiled and analyzed. Preliminary estimates place the total bill to replace all ODC equipment in Army facilities at $400 million.

Between now and Thanksgiving, there will be a series of senior staff-level meetings taking place in HQDA to determine how best to span this separation between policy and execution and develop a workable ODC elimination policy. The new policy will then be issued, and a "MACOM Summit" meeting will then be held in the Northern Virginia area. The Summit meeting will allow HQDA staff to present guidance on how to implement the new policy, and allow representatives from the MACOMs to present their questions and concerns. Current schedules call for this new policy to be issued, and the MACOM Summit meeting to be held, before the end of the year.

Answers

Obviously there aren't many easy answers, or there never would've been a program review. And the new policy and guidance haven't been developed yet. However, there are some ideas that look like they'll be significant parts of the overall solution.

One of them is a much closer cooperation between the ODC elimination effort and the Army's Energy Efficiency program. There's an increasing emphasis in DoD on energy efficiency, due in part to the Department's recent commitment to address global warming concerns by decreasing carbon dioxide emissions. For the Army in particular, three quarters of the Service's green-house gas emissions are generated from facilities operations. And there is a direct correlation for installation operations between decreasing green-house gas emissions and increasing energy efficiency.

There's also a direct connection between increasing facilities' energy efficiency and replacing CFC building chillers. A 10-15 year old centrifugal chiller using CFCs needs up to twice as much electricity for same level of cooling as a new, non-CFC chiller. With building chillers holding 90% of the CFCs installed in Army facilities, any additional funding available through energy efficiency programs could have a significant impact on the ODC elimination program.

Along the same lines, Army installations are beginning to get interested in the Department of Energy's Energy Savings Performance Contracting (ESPC) program. With the ESPC, a contractor installs a new chiller in your building (with or without other energy-saving activities in the building, such as increased insulation, improved ventilation, or energy-efficient lighting) and then operates and maintains the chiller for an agreed upon period and negotiated rate. The beauty of the arrangement is that the negotiated rate is by definition less than the cost the installation is currently paying to operate and maintain the old CFC chiller.

So the Army gets a new centrifugal chiller (owned by the government, by definition in the contract), the installation sees a decrease in operating costs (and green-house gas emissions), and the contractor makes a profit through the increased efficiency of their product.

An installation's ODC replacement costs may also be delayed by more aggressive "cascading" of CFC refrigerant. "Cascading" refers to supporting existing CFC equipment by selectively retiring older and less efficient equipment that use the same refrigerant. The CFC is recovered from the retired piece of equipment, locally recycled, and reused. This way, the installation gets the most useful service life out of their equipment, and also gets rid of the least efficient equipment first. Used aggressively, the installation can also become CFC independent -- i.e., no longer needing to buy CFC refrigerant -- while CFC prices continue to skyrocket and product becomes less and less available.

The new EPR guidance, released this summer by HQDA, also provides another potential source of resourcing installation efforts. It formally identifies all planning and inventory efforts for ODC elimination as being an environmental program requirement, or "must-fund." It also identifies as "must-fund" pollution prevention projects with a pay-back of five years or less, through which the replacement of some older CFC chiller replacements may apply.

Finally, small infusions of "starter" funding may be made available by HQDA to Army installations with thought-out ODC elimination plans, to kick-start their replacement projects and facilitate their refrigerant cascading programs.

Conclusion

As Yogi Berra notably noted, "It ain't over 'til it's over." The Army is committed to eliminating its dependency on ODCs in all applications: weapon systems, industrial operations, and facilities. However, no amount of policy and guidance will guarantee a successful program without realistic resourcing and buy-in from the user.

1997 continues to be a critical year for the Army ODC elimination at installations. By the start of 1998, the Army will hopefully be postured to expedite ODC elimination with a complimentary set of policy, guidance, and resources. Efficient and timely execution of installation plans must be an overriding Army concern, or increasing costs and shortages may have a catastrophic impact on the readiness of Army units world-wide.

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Experience with Secondary Loop Refrigeration Systems in European Supermarkets

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ABSTRACT

Because of the ever-increasing demand for users and providers of refrigeration, to be environmentally conscious, no opportunity is missed to improve the overall environmental performance of some leading European supermarket companies.

This is typified by the development and testing by several of the suppliers, specifier's and purchasers of supermarket refrigeration systems in Europe, with alternative forms of producing the desired refrigeration effect.

A small number of users are committed to secondary systems, whilst others are either evaluating or using them on a trial basis.

This paper aims to give an overall view of the current development, application and limitations, of a limited number of secondary fluids, cooled by non-hazardous and hazardous primary refrigerants, in a small number of supermarkets in Europe.

INTRODUCTION

With the ever increasing pressures on the use of, and emissions from, low or zero ODP refrigerants, especially within the E U, any successful method of minimising, or successfully influencing, the total annual emissions of <u>any</u> refrigerant, is attractive.

Whether this is solely responding to environmental pressure from Governments and/or NGO's is not obvious. There is however the straightforward issue of responding to the views of the supermarket customers, and the need to present the correct image, which sometimes means keeping up with the opposition! Whatever the incentive it has become an important issue, especially when considering new installations.

The use of secondary loop cooling systems, is seen as one solution.
In this way, regardless of the primary refrigerant selected, the total refrigerant charge of the system is reduced, when compared with the conventional direct expansion system.

There is no argument against the need to reduce emissions and the benefit of a reduced refrigerant charge in secondary loop systems, considerably assists towards this objective, particularly when the primary system is leak free.

There is a view that, in a system utilising ammonia, or a hydrocarbon (HC), as primary refrigerants, it is of paramount importance to maintain pressure integrity, and ensure freedom from leaks. It is accepted that such a system must and can be maintained leak free, cost being secondary.

It must then be equally possible to construct a system for HFC and HCFC refrigerants and ensure similar pressure integrity, taking into account inevitable minor service losses.

The selection of zero ODP, zero GWP primary refrigerant may not therefore be a main issue. There could be an environmental and operational argument for the use of HFC's as a primary refrigerant, eliminating the cost of special safety features required with Ammonia and HC's.
With this consideration, a total equivalent warming impact (TEWI) comparison becomes more meaningful, placing the emphasis on the overall energy efficiency of a secondary system design.

Secondary systems can also provide less obvious benefits. With the exception of systems using CO_2 as the secondary fluid, the secondary pipe work and fittings are subjected to relatively low operating pressures, especially when compared to CO_2 or Direct expansion designs. This can lead to reduced installation costs and much simplified strength and leak pressure testing procedures.

In the EU there is another, hidden, advantage which will eventually come to light, that of the Pressure Equipment Directive No 97/23/EC (ISBN 011 916 0927), now formally adopted, and optional until 29 May 2002. This Directive along with many other demanding requirements, introduces approval of design and manufacture by "Notified Bodies". Whilst this will mainly effect the manufacture of the primary system equipment in the factory, it will also extend to site installation, adding time and cost. Clearly the lower the operating and test pressures, the less demanding will be the effect of this Directive.

Another factor effecting all supermarkets is the need to reposition merchandising equipment, including refrigerated displays. The disconnection and repositioning of such equipment can be much simplified when dealing with the re-routing of some secondary loop systems. The complexity of any cleaning up process as a result of spillage is dependent on the fluid selected, ranging from the release to atmosphere of CO_2 to special cleaning precautions with glycol and fluids such as aggressive organic salts.

BACKGROUND

It is generally accepted that the development of secondary refrigeration systems for supermarket installations in Europe in the mid 80's, was led by Sweden who was the main innovator. Swedish users, manufacturers and contractors have supported ongoing development, have been prepared to share experiences.[1]

Early installations used calcium chloride, or hazardous ethanol or similar as the secondary fluids, cooling the intermediate temperature fixtures, with a selection of primary refrigerants, R12, R502 and eventually R22, a common choice.

Low temperature refrigeration used direct expansion designs and varied from a conventional piped system, from a central plant, to individual units at fixtures with condensers cooled by piped secondary fluids, or combinations of both arrangements.

Pipe work and flow regulating valves within the supermarkets sales area, were in general completely exposed and on view to customers (a feature not acceptable in many other countries). Corrosion was a major problem and conversion of existing systems from calcium chloride to propylene glycol was a common occurrence.

The limited progress of secondary fluid development across Europe, extended mainly from the early Swedish and later German initiatives[2], progressing to propylene glycol for intermediate systems and ethylene glycol when used for low temperature applications.

SIGNIFICANT ISSUES

On going developments in Europe are as diverse as the types of fluid suitable and available for use in supermarkets. The primary/secondary fluid combinations appear to be almost country specific, often reflecting the environmental stance of the user, allied to environmental pressure groups and in some cases governmental pressure.

In general, concerns remain regarding the capital and maintenance costs of secondary loop installations, also the overall energy consumption. However as confidence has increased, mainly as a result of operating experience with trial systems, designs have also been simplified. This fact, plus the continuing development, and introduction of new fluids, has led to a reduction in the energy penalty of new secondary systems.

The energy efficiency is particularly important when selecting the overall package covering, the primary refrigerant, the system design and the equipment manufacturer. It is of the greatest importance when a TEWI comparison is also used as the basis for that selection.

Capital cost, equipment availability, installation time and a proven record of reliability of a system, ease of maintenance, effect of fluid leakage; all feature in the selection process, indeed to some these are the main criteria for any purchase. The result in real terms is however often one reduced to a selection based on a combination of TEWI and capital cost or in some cases, only the latter.

Without exception, the introduction into a supermarket of a new secondary fluid, has been preceded by costly development. In the main, manufactures and/or contractors have provided the funds.
In the UK, a large supermarket[3] has invested considerable sums in funding "off site" development and testing[4], to prove successful operation and reliability, prior to risking a live installation.
In such developments the display case[5]and cold room cooler manufacturers[6] have also invested in designing and testing suitable coil circuitry, metering controls and product operating performance, in order to meet the customer's demands. There is therefore a hidden cost for the prospective user, and supplier, to consider.

The practical choice of primary refrigerants range from hydrocarbons, ammonia, HFC's and to a limited degree HCFC's, the selection of which is well documented.

TYPICAL EUROPEAN DEVELOPMENTS

In 1995 one leading supermarket[3] in the UK used ammonia as the primary refrigerant with a combination of propylene glycol for intermediate temperatures and a proprietary brand of silicon oil for low temperatures.
Low temperature defrost was achieved by a silicon oil loop, heated by the primary refrigerant.

The silicon heat transfer fluid used was a low viscosity liquid, essentially non-toxic and non-corrosive with good heat transfer properties. A lower volumetric heat capacity does however necessitate higher secondary flow rates, when compared with organic salt solutions.
The data sheet[7] states the product is flammable and the flash point, of this colourless liquid, is a low 47^{0}C, it also lists actions to be taken in the event of inhalation, skin contact, eye contact and ingestion. Recommendations for fire fighting measures, accidental release, disposal, handling and storage and personal protection are also detailed. This is standard data available for any similar product.

The introduction of silicon oils provided a breakthrough for low temperature secondary systems and was available on the market along with a choice of organic salt solutions. The development of CO_2 secondary fluid systems was also becoming established.

Parallel developments using commercial brands of organic salts has given a choice to the designer and user, as with all products, there are claims and counter claims as to the ideal solution.

The products readily available on the market claim to provide a stable, non-toxic, biodegradable liquid, suitable for use within the supermarket environment.
Additives to check the corrosive effects are required in all solutions, which also have relatively high pH values.

Another most interesting addition to the list of potential secondary fluids, still under development[8], is the use of flow ice at low temperatures, to which an additive, such as a potassium formate, has been added.

Flow ice, less any additive, has considerable potential when used as a source of direct refrigeration, for use "in store" supermarket preparation areas and by product suppliers. (Already demonstrated world wide on trawlers)
A Technical paper[9] presented at the Institute of Refrigeration has reported on developments with supermarkets using flow ice as a cooling medium, but its impact to date does not compare with that of organic salts. Nevertheless it merits its mention and place in the European picture on secondary fluids for supermarkets.

One of the oldest and perhaps the most common refrigerant CO_2 has been successfully applied to several supermarket installations in Sweden[10]. The development work is reported to be the initiative of a major Swedish refrigeration company, who have developed the specialist skill and know how necessary for such a design and installation.

In a recent UK technical article[11] it was claimed that "Sweden is pioneering with a new generation of supermarkets". The case reported on a 30,000-sq. ft. sales area supermarket[12] that used hydrocarbon refrigerants to cool propylene glycol for medium temperatures, and to condense CO_2, used for the low temperature system.

In basic terms, a typical installation[13] will utilise liquid CO_2 as the low temperature refrigerant, pumping it via a ring main to fixtures, where a partial change in state is induced, as some of the liquid is vapourised.
A separate and dedicated hydrocarbon refrigerant (HC) package system is used to condense the resultant CO_2 liquid/vapour mixture, prior to its return to a storage receiver, from where it is circulated to the system.
The glycol serving the intermediate temperature system is cooled by another HC refrigerant package system.

Special arrangements are made to keep the CO_2 below $-15\ ^0C$, as above this temperature the system is designed to relieve to atmosphere to avoid excessive pressure build up. With the restoration of normal pressures, the system CO_2 charge must be adjusted.

In Germany a major manufacturer[2] and contractor has over several years developed packaged secondary refrigerant systems. Although available for a

variety of refrigerants, ammonia and more recently also HC systems is a popular section of the range.

It is reported that there are various applications for these secondary systems, in general utilising glycol for intermediate temperatures and one of several brands of organic salt, for low temperature systems.

Countries such as Switzerland, Luxembourg, and Northern Italy[14] are reported to be using ammonia on a more general basis, although much has to do with the size and location of the installation when as an alternative R404A would be the choice.

In the UK a small number of users have used ammonia on a trial basis, one[15] even attempted CO_2, but those continuing to trial secondary systems are using HFC's. There is a firm view in the UK and some other countries, that further use of ammonia, or the early introduction of HC's as a supermarket primary refrigerant, is unlikely at this stage, capital cost, compliance with standards and customer safety, will all play an important part in any decision.

PRACTICAL CONSIDERATIONS

The qualified and fully trained responsible refrigeration engineer is well aware of the issues and problems associated with the use of low or zero ODP refrigeration, what ever the application, including the eventual effect of emissions on mankind.

The problems that could be associated with secondary fluids, is less obvious and not yet common knowledge in our industry.

In the UK there is a responsibility to comply with the Health and Safety at Work Regulations (H&S@W). Also under the Control of Substances Hazardous to Health (COSHH) Assessments, a responsibility to ensure that safety data sheets on such products, identifying the physical properties, are assessed and ultimately retained the H & S @W file.

The overall scheme, considering primary and secondary fluids, should be safe, efficient, practical and capable of being serviced by qualified refrigeration engineers without special training.

A full risks assessment involving, if necessary, the appropriate authorities, should be carried out, covering all aspects of design, installation, operation and maintenance.

The physical characteristics of a product should be established and considered in any selection process, plus any design constraints. This includes items such as flash point, effect on system materials, corrosive properties, injurious to exposed

skin and eyes, air born hazards, affinity for moisture absorption, effect of spillage on floors, products, drainage systems and associated materials. The acceptability of any fluid colouring should also be addressed.

Basic design considerations should include the routing of pipe lines and access to isolating, drain and control valves, also the protection of these components when their location is vulnerable and liable to damage, especially where a rupture could cause secondary fluid to be sprayed over product or public areas. Above all, not neglecting the method to be used to fill the system. The question of the secondary fluid pump materials, especially the gland seals must be addressed, to establish that they suitable.

The question of any special maintenance requirements should be raised. For example, is any special clothing necessary to protect operatives? How would drained or spilled fluid be disposed of? Would the waste be hazardous, where and how would it be disposed? Would isolating and control valves require periodic operation and examination? If so would they be accessible? Who would be responsible for the replacement or renewal of valve and pipe insulation, and so on!
Clearly many of these points will be eliminated in any examination, but historically all have, at some time, been an issue.

A RECENT SECONDARY REFRIGERANT DESIGN

A major UK supermarket[3] made the investment to investigate and analyse secondary system performance and have permitted this information to be released.
The first trial,[16] already mentioned, using ammonia as the primary refrigerant, propylene glycol for intermediate and silicon oil for low temperature, has been well reported. There is no disguising the very high cost of the installation and resultant excessive energy consumption.

Many lessons were learned and after much planning, a second trial in a 28,000 sq ft sales area store[17] was approved. This was designed as a simple, safer, more acceptable, practical solution. All unnecessary frills were eliminated and the refrigeration system was built and commissioned with out incident.

Plant Arrangement

Two, dual temperature, factory assembled packages[18] used R407C as the primary refrigerant. System designers[19] and plate heat exchanger manufacturers[20] arranged circuits to maximise the benefits of the temperature glide features of R407C. The total intermediate system heat extraction capacity was 234kW, with a low temperature capacity of 44kW.

The primary refrigerant charge of R407C for each systems was 150 kg.

The liquid receiver located below each system air-cooled condenser was designed for full pump down capacity of that system. A permanent automatic leak detection system was employed in the plant room.

Two plate heat exchangers were designed into each package, one selected to cool 50% of the intermediate temperature, the second to cool 50% of the low temperature fluid.
Electronic expansion valves regulate the liquid refrigerant on each plate heat exchanger. Remote, and locally accessible, data logging and control is provided by a refrigerant management system covering the plant room and sales area fixtures.

The secondary fluid for both high and low temperature applications is a proprietary brand of organic salt[21], with densities having freezing points of –30°C and –45°C respectively. Flow temperatures to fixtures are –9°C for intermediate and –32°C for low temperature pumped systems.
A total of 4500 litres of fluid was charged into the pressurised system, which has a small, permanent, top up pumping system incorporated with the pump station. Shared pump stand-by is also incorporated.

Display case and cold room evaporator temperature control, was a simple on/off arrangement via a solenoid valve in each fixture, operated through individual electronic controllers. Defrost was "off cycle" in dairy and produce cases, low temperature cases use electrical heater elements, control was time start with standard temperature termination, time override back up.

OPERATIONAL EXPERIENCE

Frost build up on coil surfaces was even and uniform, air distribution through frosted heat exchangers was even, reportedly producing a stable air discharge temperature profile.
Temperature difference between coolant flow and return was smaller than anticipated, and allowed the inlet temperatures to be raised slightly above design values, this benefit reflects on the compressor operating temperatures and pressures, also the energy consumed.
The flywheel effect of the circulating fluid tends to dampen temperature fluctuations in the system during operation, and during maintenance or short periods of service or repair. The subsequent recovery is rapid.

The temperature performance of display cases and cold rooms satisfied the high standard set by the user.
Defrost is reported to continue for longer than originally envisaged, but no adverse effects on product have been experienced.
Recovery after defrost is noticeably rapid, and with little effect on product temperature during defrost, a good temperature profile is produced.

Service engineers[22], having acclimatised to the different operating characteristics and maintenance procedures, report their confidence in, and liking for, the system. The responsibility for regular checks of the secondary fluid is however passed to the chemical supplier, who carries out an analysis at regular intervals.

Measurement to date shows that the overall energy consumption, compared with a similar direct expansion system selected from the same area of the country, is only marginally higher for the secondary system during the initial period of operation. However a meaningful energy audit should, to be effective, extend over a complete year, to reflect all climatic variations.

There are opportunities to lower the overall energy consumption, mainly with adjustments within the plant room.

The measured flow and return temperature difference relative to design may permit a reduction in flow rate to some or all fixtures, which may also be combined with an increase in the flow temperatures. (Future designs may incorporate variable speed pumps)
Utilising the full potential of the refrigeration management and control system[23], designed to achieve optimum energy efficiency, will also provide opportunities for improvement.

But these factors have to set against the realisation that the prime function of the system is to provide reliable temperature stability and uninterrupted service to the supermarket and its customers.
There will always be a dilemma. Although the supermarket system is operating trouble free, there is a natural tendency for the technician to make non-essential adjustments, in an attempt to further improve operation, not always with success.

As experience is gained and shared with others, confidence with this type of system will increase, and designs incorporating the many lessons, some already learned, others noted in this paper, could achieve the level of security demanded.

CONCLUSION

It is not possible to give a complete European overview owing to the almost country specific approach to primary and secondary refrigerants, plus the difficulty in obtaining accurate information.

There is a considerable interest in secondary refrigerant systems and applications, and this has been clearly identified by some designers, manufacturers and contractors as a sound commercial opportunity.

Making the decision on the primary refrigerant gives several options, but the choice of secondary fluid falls into two camps, liquids that change state during the cooling process and those that remain as liquids, during the cooling process.

Investment in research and development has, in all cases, been necessary to gain the experience, essential if the product/system is to be successfully marketed and safely applied.

Ready access to such information is usually restricted, limiting its application to a wider market, thereby reducing the pace of progress.

As the confidence of both user and contractor grows, along with a cost effective, proven system safety, reliable and efficient operation, and effective temperature control, there may be a steady expansion in this sector of the refrigeration industry.
However, the conventional system is still favoured by the majority of supermarkets as their basic design solution.

There is no doubt that the best promoters of the secondary refrigerant principle are the engineers who install, service and maintain, the simple and safe secondary system as described above.

Acknowledgements

1 Electrolux Commercial Refrigeration Data & TotalKyl Malmo Sweden
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3 Sainsbury's Supermarkets Ltd
4 Westward Refrigeration Ltd
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10 Bonus AB Sweden
11 Refrigeration and Air Conditioning Magazine Page 34 September 1997
12 AG Favor Vala Centrum Sweden
13 ABB Stal-Litzell
14 Linde Refrigeration Data
15 Marks & Spencer Scotland
16 Sainsbury's Supermarkets Ltd Horsham England
17 Sainsbury's Supermarkets Ltd Kirkaldy Scotland
18 Jerome Engineering Group UK
19 L A Associates Consulting Engineers
20 Alfa Laval Thermal Ltd
21 Hycool 30 & Hycool 45 Hydro Chemicals Ltd
22 Westward Refrigeration Edinburgh Scotland
23 Elm Ltd Glasgow Scotland