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AEC RESEARCH AND DEVELOPMENT REPORT

FURTHER STUDIES OF AMINES AS EXTRACTANTS FOR URANIUM FROM ACID SULFATE SOLUTIONS

J. G. Moore
K. B. Brown
C. F. Coleman

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FURTHER STUDIES OF AMINES AS EXTRACTANTS FOR URANIUM FROM ACID SULFATE SOLUTIONS

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ABSTRACT

Since the first report on the use of amines as uranium extractants (ORNL-1734) over eighty additional organo-nitrogen compounds have been examined for their ability to extract uranium from aqueous solutions, particularly sulfate solutions, of the types usually encountered in uranium ore processing. As before, the more promising of these (as well as other compounds previously reported) have been examined further with respect to other characteristics essential to practical application, i.e., reagent loss to the aqueous phase, compatibility with practicable diluents, influence of commonly present anions, reagent stability, sufficient selectivity for uranium, adequate phase separation properties, compatibility with practicable stripping methods, etc. The potential cost and availability of the reagents have also been considered. Several of the newer reagents tested, i.e., certain secondary and tertiary amines, have shown even greater promise as practicable extraction agents than many of the promising compounds previously tested.

In addition to the work with sulfate liquors, cursory studies have been made of uranium extraction from fluoride and sulfate-fluoride solutions. Extractions of other metals from sulfate liquors, i.e., titanium and thorium, have been briefly examined.

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I. INTRODUCTION

The investigation and evaluation of organonitrogen compounds for the separation of uranium from various aqueous systems has been underway at this laboratory since early 1952[1]. The primary concern of this work has been the possible practical application of such compounds (particularly the amines) to large scale extraction and separation of uranium from aqueous solutions which may also contain a large variety of other ions. Because of the frequent use of sulfuric acid in uranium raw material processing, most of the extraction studies have been made on uranium-bearing sulfate solutions.

As described previously[2] the work conducted at this laboratory may be divided into three categories: (a) screening tests aimed at the discovery and selection of reagents most likely to be useful in practical application, (b) process development studies, and (c) studies of the fundamental factors which govern the extraction of acids, uranium, and other metals.

In the screening tests a systematic approach to the problem is used so that those reagents showing the least promise may be eliminated in a stepwise manner. In initial experiments, each reagent is tested for its ability to form extractable uranium complexes from aqueous solutions of the type most likely to be encountered in process operations. The most acceptable reagents from these tests are next examined in regard to their ability to meet other specifications of importance to a successful solvent extraction process, e.g., compatibility with practicable solvents, acceptably low loss to the aqueous phase through solubility, sufficient selectivity for uranium, adequate extraction coefficients over a range of solution compositions, compatibility with practicable stripping methods, adequate phase separation properties, reagent stability, etc. The potential costs and availability of the reagents are also considered. By conducting such experiments in sequence, those compounds which "fail" in one series of tests are eliminated from intensive consideration in a subsequent series.

Results from such screening studies on over 100 different reagents were reported in ORNL-1734. This report will describe further tests on the more promising of these reagents as well as tests on some 80 additional compounds.

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The compounds showing greatest promise in the screening studies are next included in the laboratory process development program wherein a closer evaluation is made of operational characteristics, reagent usage and stability, and optimum process schemes for the extraction and stripping cycles. Those compounds continuing to show promise are then submitted to the Engineering Group for evaluation in a larger scale process test facility. Several of the compounds examined in the laboratory and larger-scale process tests have given successful performance. Reports describing these studies are being prepared and will be issued shortly. Separate reports are also being prepared describing the results from the fundamental studies of amine extraction that have been completed thus far.

In addition to sulfate liquors, cursory tests have also been made with solutions containing other anions. Uranium extractions from nitrate, chloride and phosphate solutions were reported previously[2]. Tests with fluoride and carbonate solutions are described below. In the latter case, the strong base quaternary ammonium salts have been of interest as extractants rather than the weak base amines.

In addition to uranium, some attention has been given to the possible extraction of other metals from sulfate solutions. Extraction tests on vanadium, zirconium, thorium, etc. have been briefly described[2] and the use of primary amines in the processing of thorium ores has been proposed[3]. Other studies on uranium-thorium separation and titanium extractions are reported here.

II. DESCRIPTION OF COMPOUNDS

Most of the organonitrogen compounds discussed in this report were obtained from commercial sources such as the Armour Chemical Division of Armour and Company, Carbide and Carbon Chemicals Company, B. F. Goodrich Chemical Company, Rohm and Haas, Pfister Chemical Works, etc. Other compounds were prepared at this laboratory using methods similar to those described in ORNL-1734, Appendix B.

The reagent purity of the organonitrogen compounds is often difficult to determine by direct measurement and difficult to describe in specific terms. In previous work[2], reasonable approximations of the "purity levels" have been obtained by relying upon several sources of information, as for example, equivalent weights by non-aqueous titration, carbon-hydrogen-nitrogen analyses, distillation ranges, solubility measurements, manufacturer's data, etc. These sources of information have also been used in the present studies. In addition, further indications of the "purity level" for some of the reagents have been obtained by determining primary, secondary and tertiary amine contents according to a differential titration method based on that proposed by Fritz and others[4]. The purity level of compounds investigated may be found in Appendix C. The indicated "purity range" for the amines is from 75% to 99% with most of the compounds being greater than 90%. The quaternary compounds range from 70-95% and, although little information is available, the range for the miscellaneous nitrogen compounds is probably about the same.

As has been pointed out previously, the nature and distribution of impurities found in the various reagents are dependent upon several factors such as the type of compound prepared, the purity of the starting materials and the preparation path. Common contaminants to be expected are unreacted starting materials, water, alcohols, and other organonitrogen compounds of the same or a different class. Some of these would react with uranium in a manner analogous to that of the major component whereas others would be essentially inert in the extraction process. Although it is apparent from the above that some of the reagents were not of reagent grade, they were considered acceptable for screening studies since these were concerned with relatively large differences of performance between different reagents.

III. EXPERIMENTAL

A. PRELIMINARY URANIUM EXTRACTION TESTS

In the investigation of the organonitrogen compounds as reagents suitable for the extraction of uranium from various aqueous systems, the preliminary evaluation consists of a series of simple extraction tests designed to aid in the selection of compounds most likely to be useful in a practicable application. Since the first report on this subject (ORNL-1734, Table 1), many other, different reagents have become available. These as well as new batches of previously tested compounds, e.g., C&CCC 16F27, have been examined using the same procedure and conditions as before (cf. ORNL-1734, page 6).

> "..... In the initial tests, an acidic uranyl sulfate solution, U ~1 gm/l, $SO_4^{=}$ = 1 M, pH ~1, has been contacted in a separatory funnel with equal volumes of the following reagent-diluent mixtures: (a) 0.1 M reagent in chloroform, (b) 0.1 M reagent in benzene, and (c) 0.1 M reagent in benzene, prewashed with an acid sulfate solution. After five minutes of vigorous shaking the organic and aqueous layers were separated and the extractions were measured by fluorometric determination of the uranium in each phase.
>
> "When the extractions with (c) were significantly less than those with (b), it was assumed that the compounds were appreciably soluble in aqueous solutions and interest in these particular reagents diminished. In cases where loss by aqueous solubility was not evident with 0.1 M reagent and the reagent showed sufficient extraction to be of interest, the tests were repeated using 0.01 M reagent as more sensitive to solubility loss. (The latter tests served only to amplify the solubility losses; they were not particularly useful for comparisons of the extraction power of different reagents since the organic phase at this low reagent concentration was frequently approaching saturation with uranium.)"

The results from these screening tests, made since the last report, are given in Table 1.

In addition to the tests described, the initial screening type studies have also been extended to include kerosene as the diluent. Studies with kerosene were made

Table 1

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

A. Primary Amines

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
Furfuryl	0.1	0.98	nil	nil	nil	nil	nil	nil	Good
Octyl (tertiary)	0.1	0.98	nil	nil	nil	nil	nil	nil	Good
Dehydroabietyl (Rosin Amine D)	0.1	0.98	ppt.		ppt.		ppt.		----

B. Secondary Amines

Di(OxoDecyl)	0.01	0.98	nil	nil	23		28		Good
	0.1	0.98	96	26	96	23	96	21	Good
Di(2-butyloctyl)	0.01	0.98	4		41		39		Good
	0.1	0.98	85	6	99	130	99	71	Good
Bis(1-methyl-4-ethyloctyl)	0.01	0.92	24	-	39	-	39	--	Good
	0.1	0.92	92	12	98	27	95	20	Good
N-(2-ethylhexyl)-1-isobutyl-3,5-dimethylhexyl	0.1	0.92	75	3	99	76	98	45	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

B. Secondary Amines (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
Di(Tridecyl B)	0.01	0.98	12		38		32		Good
(Cmpd. 162A)	0.1	0.98	83	5	83	5	74	3	Good
Di(Tridecyl B)	0.01	0.92	16		38		31		Good
(Cmpd. 218A)	0.1	0.92	87	6	69	2	60	1.5	Good
Di(Tridecyl P)	0.01	0.92	--	--	39		39		Good
(Cmpd. 227A)	0.1	0.92	98	42	99	120	98	63	Good
R&H 9D-178	0.01	0.98	13		37		41		Good
(Cmpd. 193B)	0.1	0.98	87	8	99	74	98	56	Good
R&H 9D-178	0.01	0.92	12		31		32		Good
(Cmpd. 193C)	0.1	0.92	88	8	99	66	98	45	Good
C&CCC 16F27	0.01	0.92	2		22		22		Good
(Cmpd. 30B)	0.1	0.92	45	0.8	91	10	87	7	Good
Armeen 2S	0.01	0.98	29		37		37		Good
(Cmpd. 151A)	0.1	0.98	98	50	99	100	99	70	Good
Armeen 2T	0.01	0.98	26		42		40		Good
(Cmpd. 152A)	0.1	0.98	99	150	99	125	99	70	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

B. Secondary Amines (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
7-Aminomethyl-1,4-dimethyl-1,6-dioxabicyclo-3.2.1-octane	0.1	0.92	< 1	< .1	nil	nil	nil	nil	Good
Benzyllauryl	0.01	0.92	35		37		41		Good
	0.1	0.92	99	340	99	130	99	110	Good
N-benzyl-1(3-ethylpentyl)-4-ethyloctyl	0.01	0.92	26		40		41		Good
	0.1	0.92	99	110	99	>1000	99	>1000	Good
Phenyl-β-naphthyl	0.1	0.98	< 1	< .1	nil	nil	nil	nil	Good
p-Isopropoxydiphenyl	0.1	0.98	nil	nil	nil	nil	nil	nil	Good
Phenylethanol	0.1	0.98	nil	nil	nil	nil	nil	nil	----
α-Methylbenzylethanol	0.1	0.98	nil	nil	nil	nil	nil	nil	Good
o-Tolyldiethanol	0.1	0.98	nil	nil	nil	nil	nil	nil	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

C. Tertiary Amines

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
N,N-dimethyl-Soyamine	0.1	0.98	Emulsion		Emulsion		Emulsion		----
Di(Nonyl B)butyl	0.1	0.92	72	3	99	85	98	60	Good
Dihexyl(Tridecyl B)	0.01	0.98	2		33		35		Good
	0.1	0.92	59	1.5	98	70	98	60	Good
Tri(Tridecyl B)	0.01	0.98	< 1		3		3		Good
	0.1	0.98	6	.1	50	1	42	.7	Good
N-Benzyl-bis(2-ethylhexyl)	0.1	0.92	< 1	<.1	1	<.1	< 1	<.1	Good
Benzyldilauryl	0.01	0.92	4		35		37		Good
	0.1	0.92	80	4	98	48	98	40	Good
Dibenzyllauryl	0.01	0.92	< 1		< 1		< 1		Good
	0.1	0.92	63	1.7	60	1.5	62	1.6	Good
Phenylmethyl-ethanol	0.1	0.98	nil	nil	nil	nil	nil	nil	----

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

C. Tertiary Amines (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
Phenyldiethanol	0.1	0.98	nil	nil	nil	nil	nil	nil	----
Phenylethylethanol	0.1	0.98	---	---	---	---	2	.1	----
α-Methylbenzyl-diethanol	0.1	0.98	nil	nil	< 1	<.1	< 1	<.1	Good
m-Tolyldiethanol	0.1	0.98	nil	nil	< 1	<.1	< 1	<.1	Good
Di(2-ethylhexyl)-ethanol	0.1	0.98	---	---	59	1.5	36	.6	Good

D. Miscellaneous Nitrogen Compounds*

Anilide of BON*	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
m-Nitranilide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
p-Nitranilide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Miscellaneous Nitrogen Compounds (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
m-Chloranilide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
p-Chloranilide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
o-Toluidide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
p-Toluidide of BON	Sat.	0.98	nil	nil	2	< .1	nil	nil	Good
4-Chloro-o-toluidide of BON	Sat.	0.98	2	< .1	nil	nil	nil	nil	Good
5-Chloro-o-toluidide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
m-Xylidide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
p-Anisidide of BON	Sat.	0.98	< 1	< .1	nil	nil	---	---	Emulsion in $CHCl_3$

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Miscellaneous Nitrogen Compounds (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
o-Anisidide of BON	Sat. ($CHCl_3$ = < 0.06 M)	0.98	< 1	< .1	< 1	< .1	< 1	< .1	Good
Chlor-Anisidide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
Di-Anisidide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
2,4-Dimethoxy-4-chloro Anilide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
2,5-Dimethoxy-4-chloro Anilide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Fair
2,5-Dimethoxy Anilide of BON	Sat. (< .05 M)	0.98	nil	nil	nil	nil	nil	nil	Good
o-Phenetidide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Miscellaneous Nitrogen Compounds (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
p-Phenetidide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
α-Naphthyl Amide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Fair
β-Naphthyl Amide of BON	Sat.	0.98	nil	nil	nil	nil	nil	nil	Fair
α-Picoline	0.1	0.98	2	< .1	nil	nil	nil	nil	Good
2-Methyl-5-ethyl-pyridine	0.1	0.98	nil	nil	nil	nil	nil	nil	Good
2-Vinyl-5-ethyl-pyridine	0.1	0.98	nil	nil	nil	nil	nil	nil	Good
Alkyl pyridines H.B.	0.1	0.92	2	< .1	---	---	1	< .1	Good
N-Ethylpiperidine	0.1	0.92	nil	nil	nil	nil	nil	nil	----
N-Decylpiperidine	0.1	0.92	98	48	5	< .1	<1	< .1	Fair

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Miscellaneous Nitrogen Compounds (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
2,5-trans-Dimethylpiperazine	0.1	0.92	nil	nil	nil	nil	nil	nil	Good
o-Xylidine	0.1	0.92	nil	nil	nil	nil	nil	nil	----
Acetoacetyl-o-tolidine	Sat.	0.98	2	< .1	nil	nil	nil	nil	Good
p-Anisidide of 3-hydroxybenzo-carbazole-2-carboxylic acid	Sat.	0.98	< 1	< .1	nil	nil	nil	nil	Benzene Poor
p-Methoxy-o-methylanilide of 3-hydroxybenzo-carbazole-2-carboxylic acid	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
o-Toluidide of 2,3-hydroxyanthra-cenecarboxylic acid	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Miscellaneous Nitrogen Compounds (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
2,5-Dimethoxyanilide of 2-oxydibenzofurane-3-carboxylic acid	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
p-Chloroanilide of 2-hydroxycarbazole-3-carboxylic acid	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
Bis-2,4-dimethoxy-3-chloranilide of terphthalyldiacetic acid	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
Trimethyldihydroquinoline polymer	0.1	0.98	18	0.2	< 1	< .1	nil	nil	Good
Rhodanine	Sat.	0.98	---	---	nil	nil	nil	nil	----
N-Nitrosodiphenylamine	0.1	0.98	nil	nil	nil	nil	nil	nil	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Miscellaneous Nitrogen Compounds (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
N-"Tallow"-morpholine	0.1	0.98	97	37	95	19	99	120	Benzene Poor
N-"Coco"-morpholine	0.1	0.98	98	54	nil	nil	nil	nil	Benzene Poor
N-Phenyl-morpholine	0.1	0.98	nil	nil	nil	nil	nil	nil	Good
N-Aminopropyl-morpholine	0.1	0.98	1	< .1	nil	nil	nil	nil	Good
Di-ß-naphthyl-p-phenylenediamine	Sat.	0.98	nil	nil	nil	nil	nil	nil	Good
Ammonyx CO	0.1	0.92	25	.3	Insol. in Benzene		Insol. in Benzene		Emulsion in Aqueous
2-Mercaptobenzimidazole	Sat. (< .05 M)	0.98	nil	nil	nil	nil	nil	nil	Good
2-Allylthiobenzothiazole	0.1	0.98	nil	nil	nil	nil	nil	nil	Good

Table 1 (Cont'd.)

PRELIMINARY EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH ORGANONITROGEN COMPOUNDS

D. Miscellaneous Nitrogen Compounds (Cont'd.)

Amine	Conc. M	Init. Aq. pH	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene (Prewashed) Extn. %	Benzene (Prewashed) E_a^o	Phase Separation
2-Vinylthio-benzothiazole	0.1	0.92	nil	nil	nil	nil	nil	nil	Good
Hexamethylphos-phoramide	0.1	0.98	nil	nil	nil	nil	nil	nil	Good

Extraction Conditions: Organic contacted with aqueous (1:1 ratio) containing ~1 g/l uranium and 1 M SO_4 for 5 minutes. Phases then allowed to separate and analyzed for uranium.

*BON = ß-Hydroxynaphthoic acid.

**Saturated solutions unless otherwise noted contained less than 0.03 M reagent.

on the amines previously reported (Table 2, ORNL-1734) but at that time the plan of investigation consisted of comparing various diluents after the reagent had been found favorable by the initial screening procedure. Table 2 shows the results of tests using 0.01 or 0.1 M solutions of reagent in kerosene, omitting reagents which were either insoluble in the diluent, or gave no extraction.

The more important observations and conclusions drawn from examination of the data presented in Tables 1 and 2, in conjunction with the previous studies (ORNL-1734, Table 1), are itemized below.

Primary Amines

1. Only three additional reagents have been examined and none of these proved to be effective extracting agents. Primene JM-T and C&CCC 21F81, i.e., 1(3-ethylpentyl)-4-ethyloctylamine, continue to be the most acceptable primary amines of those tested.

Secondary Amines

1. Previously it was reported that several saturated alicyclic and branched-chain amines gave excellent extractions without interference from emulsion formation. Most of the particular compounds tested, however, showed appreciable loss to the aqueous phase indicating that a reagent of higher molecular weight would be more suitable. Although little progress has been made with the alicyclic compounds, several of the newly acquired higher molecular weight branched-chain reagents have shown considerable promise in the screening tests. The following of these amines, di-2-butyloctyl, bis(1-methyl-4-ethyloctyl), di(Tridecyl P), and N-2-ethylhexyl-1-isobutyl-3,5-dimethylhexylamine, have given good extractions and phase separations with either kerosene or benzene as the diluent. Further comparisons of these compounds, in regard to other essential properties, will be given in subsequent sections.

2. In the initial evaluation of secondary amines in which one of the alkyl groups carried an aromatic substituent two of the three amines examined, tetradecyl(3-phenylpropyl)amine and N-(2-ethylhexyl)-α-methylbenzylamine, gave good extraction performance (ORNL-1734, page 19).

Table 2

EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH KEROSENE SOLUTIONS OF ORGANONITROGEN COMPOUNDS

Primary Amines	Conc. M	Init. Aq. pH	% Extn.	E_a^o	Phase Separation
Dehydroabietyl (Rosin Amine D)	0.1	0.98	Waxy ppt.		----
Secondary Amines					
Di(OxoDecyl)	0.01	0.98	24		Good
	0.1	0.98	Third Phase		Good
Di(2-butyloctyl)	0.01	0.98	36		Good
	0.1	0.92	> 99	400	Good
Bis(1-methyl-4-ethyloctyl)	0.01	0.92	37		Good
	0.1	0.92	89	8	Good
N-(2-ethylhexyl)-1-isobutyl-3,5-dimethylhexyl	0.1	0.92	99	180	Good
Di(Tridecyl B) (Cmpd. 162A)	0.01	0.98	30		Good
	0.1	0.98	Third Phase		Poor
Di(Tridecyl B) (Cmpd. 218A)	0.01	0.92	40		Good
	0.1	0.92	Third Phase		Poor
Di(Tridecyl P) (Cmpd. 227A)	0.01	0.92	38		Good
	0.1	0.92	99	84	Good
R&H 9D-178 (Cmpd. 193B)	0.01	0.98	39		Good
	0.1	0.98	99	90	Good
R&H 9D-178 (Cmpd. 193C)	0.01	0.92	31		Good
	0.1	0.92	99	97	Good
16F27 (Cmpd. 30B)	0.01	0.98	32		Good
	0.1	0.98	98	50	Good
Armeen 2S (Cmpd. 151A)	0.01	0.98	32		Good
	0.1	0.98	97	30	Fair

Table 2 (Cont'd.)

EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH KEROSENE SOLUTIONS OF ORGANONITROGEN COMPOUNDS

Secondary Amines	Conc. M	Init. Aq. pH	% Extn.	E_a^o	Phase Separation
Armeen 2T (Cmpd. 152A)	0.01	0.98	--		Fair
	0.1	0.98	97	30	Org. Cloudy
Benzyllauryl	0.01	0.92	Third Phase		Good
	0.1	0.92	"	"	Good
N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl	0.01	0.92	38		Good
	0.1	0.92	> 99	> 1000	Good
Tertiary Amines					
Di(Nonyl B)butyl	0.1	0.92	Third Phase		Good
Di(Nonyl B)butyl with added alcohol[a]	0.1	0.92	98	58	Good
Dihexyl(Tridecyl B)	0.01	0.98	25		Good
	0.1	0.92	Third Phase		Good
Dihexyl(Tridecyl B) with added alcohol[a]	0.1	0.92	98	64	Good
Tri(Tridecyl B)	0.01	0.98	10		Good
	0.1	0.98	87	7	Org. Sl. Cloudy
N-benzyl-bis(2-ethylhexyl)	0.1	0.92	1	< 0.1	Good
Benzyldilauryl	0.01	0.92	5		Good
	0.1	0.92	94	15	Poor
Dibenzyllauryl	0.01	0.92	1		Good
	0.1	0.92	24	0.3	Good
Di(2-ethylhexyl)-ethanolamine	0.1	0.98	Third Phase		Good

Table 2 (Cont'd.)

EXTRACTION TESTS FROM SULFATE SOLUTIONS

WITH KEROSENE SOLUTIONS OF ORGANONITROGEN COMPOUNDS

Tertiary Amines	Conc. M	Init. Aq. pH	% Extn.	E_a^o	Phase Separation
α-Methylbenzyl-diethanolamine	0.1	0.98	8[b]	< 0.1	Good
Misc. Nitrogen Compounds					
Anilide of BON[c]	Sat.	0.98	< 1	< 0.1	Good
o-Anisidide of BON[c]	Sat.	0.98	< 1	< 0.1	Good

Extraction Conditions:

Organic contacted with aqueous (phase ratio 1:1) containing ~1 g U/l and 1 M SO_4 for 5 minutes. Phases then allowed to separate and analyzed for uranium.

a) Kerosene diluent modified with 2 v % capryl alcohol.

b) % Extraction by α-methylbenzyldiethanolamine based on analysis of head and raffinate whereas others are based on raffinate and extract.

c) BON = β-Hydroxynaphthoic acid.

Recently two additional compounds have been checked, benzyllaurylamine and N-benzyl-1(3-ethylpentyl)-4-ethyl-octylamine. The first of these gave good extractions and separations in benzene (very good in chloroform) but produced a third phase when used in kerosene unless a small amount of a diluent extender such as a long-chain alcohol had been added to the diluent (see Table 4). The latter reagent, in either kerosene or benzene, gave much higher uranium extraction coefficients than have been obtained with any other organonitrogen compound previously tested. Phase separations were also extremely rapid and clean. In view of this behavior, a more complete investigation is being made of this compound as well as other amines of similar structure.

3. Three reagents have been examined in which one or both of the alkyl groups is unsaturated. Armeen 2S and 2T are mixtures of secondary amines prepared from soyoil and tallow, with both groups unsaturated. Rohm and Haas 9D-178 (dodecenyl Primene 81) has one alkyl group unsaturated and both chains highly branched. All three of these reagents gave promising extractions in the preliminary screening procedure. As will be shown later, the Rohm and Haas material is the preferable reagent due to better phase separations and high organic miscibilities of the alkyl ammonium salts with kerosene and other diluents.

4. A new batch of C&CCC 16F27, bis(1-isobutyl-3,5-dimethylhexyl)amine, gave somewhat better uranium extractions than obtained with the previous batch tested (see Table 1, ORNL-1734). Also, like some other reagents tested (see below), the extractions were better with kerosene than with benzene as the diluent. Since this compound has excellent selectivity properties, and also possesses other properties essential to a good extractant, more intensive studies are being made.

Tertiary Amines

1. Heavy emulsions were obtained in tests with N,N-dimethyl-Soyamine. This behavior is like that noted earlier for dimethyl-n-octadecylamine.

2. The unsymmetrical tertiary amines, di(Nonyl B)-butyl- and dihexyl(Tridecyl B)-, gave good extraction performance in benzene but formed third liquid phases when used in kerosene. This is analogous to the performance of compounds with similar structure examined previously. In

continued analogy, good extraction performance would be expected with these compounds when used in aromatic petroleum fractions such as Amsco D-95 and Amsco G, or when used in kerosene modified with a small amount of alcohol (see Table 2).

3. The additional highly branched symmetrical tertiary amine tested, tri(Tridecyl B)amine was a poor uranium extractant. This behavior was expected in view of the poor extractions obtained previously with tri(2-ethylhexyl)- and di(2-ethylhexyl)laurylamine.

4. The recent tests have included three high molecular weight tertiary amines in which one or more of the alkyl groups carries an aromatic substituent, viz., benzyldilaurylamine, dibenzyllaurylamine, and N-benzyl-bis(2-ethylhexyl)amine. The first of these reagents gave fair extractions of uranium (benzene > kerosene) and further evaluations are being made. The latter two reagents were poor extractants, resembling the highly branched (sterically hindered) aliphatic tertiary amines such as tri(2-ethylhexyl)-, tri(Tridecyl B)-, and di(2-ethylhexyl)laurylamine.

General

1. The importance of structural (steric) effects on the complexing ability of the amines was indicated in previous extraction studies. Some of the additional results reported above serve to corroborate the observations made at that time. With the tertiary amines, for example, it was noted previously that extractions were impaired when two or more of the alkyl radicals were branched in close proximity to the nitrogen. Confirming this are the recent results showing poor extractions with tri(Tridecyl B)amine. In addition, and probably similarly, poor extractions were obtained with dibenzyllaurylamine and N-benzyl-bis(2-ethylhexyl)amine in contrast to fair extractions with benzyldilaurylamine. Among the secondary amines, further indication of structural effects was given by the superiority of di(Tridecyl P)amine (a tetrapropylene derivative) over di(Tridecyl B)amine (a tri-isobutylene derivative). A more detailed discussion of the effects of amine structure on uranium extraction, selectivity, diluent compatibility, etc. will be given later in a separate report.

2. The extraordinary high extractions with N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine present an area for

further study. Additional work with this and similar compounds will include studies of compound structure, and also of the suitability of different diluents for different structures. On the basis of general observations of the amine extractants, it is felt that effects from the latter may be of an importance equal to those from changes in structure alone.

3. Comparison of the results with chloroform, benzene, and kerosene show again that the nature of the solvent can have an important influence on the extraction process, the magnitude and direction of which is not necessarily the same with different amines. Extractions with most of the amines tested previously were lower in kerosene than in benzene. However, many of the newer reagents have given about equivalent performance with the two solvents, and in at least some cases the performance in kerosene appeared markedly superior, e.g., tri(Tridecyl B)amine, N-(2-ethylhexyl)-1-isobutyl-3,5-dimethylhexylamine and possibly di(2-butyloctyl)amine*. Extractions with the amines in chloroform were much the same as reported earlier for similar compounds. In most cases, the polar chloroform appeared to interfere with the extraction (possibly by competition for the amine, see ORNL-1734, p. 21) whereas in some cases the extractions were as good or better than those with benzene as the diluent. Reasons for these differences are not completely understood and may eventually receive further study. Such studies, of course, would be of academic rather than practical interest since chloroform would not be a desirable solvent for process application.

4. The extractions from the sulfate liquors in Tables 1 and 2 were accompanied, as described earlier, by a small increase in the aqueous pH. The magnitude of the changes was similar to those described on p. 22, ORNL-1734.

5. On the basis of the recent screening studies, the following additional compounds have been considered worthy of further examination:

With kerosene as the diluent: N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine, di(2-butyloctyl)amine, Rohm and Haas 9D-178, N-(2-ethylhexyl)-1-isobutyl-3,5-

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*Extractions with this reagent were quite high in both instances and the difference in extraction coefficients noted may be less significant due to lower reliability in analysis of raffinates containing very small amounts of uranium.

dimethylhexylamine, di(Tridecyl P)amine, and possibly Armeen 2S, Armeen 2T, benzyldilaurylamine and bis(1-methyl-4-ethyloctyl)amine. Further studies with tri(Tridecyl B)amine are not contemplated both because of the low extraction efficiency and the fact that this compound is an extremely unlikely possibility for eventual commercial supply.

With aromatic diluents, or kerosene containing alcohol: All of the compounds listed above plus di(Nonyl B)butylamine, dihexyl(Tridecyl B)amine, benzyllaurylamine, and possibly di(OxoDecyl)amine.

Miscellaneous Organonitrogen Compounds

Organonitrogen compounds other than the simple amines or quaternary ammonium salts are classified in the screening tests as "miscellaneous compounds." None of these compounds tested previously were successful enough to be practicable, although a few such as "Duomeen S," cetyldimethylamine oxide, heptadecylglyoxalidine, etc. did show some extraction. Since that time many additional compounds have been examined (Table 1). However, as before, most of the reagents were those which happened to be at hand or easily obtainable and do not represent a complete cross section of possible organonitrogen compounds. Indeed, most of the organic solutions probably did not contain enough reagent to extract any uranium even if it were possible, since many of the compounds possessed very limited solubilities in the diluents and others had such a low molecular weight that most of the reagent was probably lost to the aqueous phase. A few reagents that did show extractions also showed difficulty in phase separation and solvent compatibility (e.g., N-decylpiperidine, N-"tallow" morpholine, and N-"coco" morpholine). Consequently, the results merely suggest again that some organonitrogen compounds, other than the simple amines, may prove satisfactory for uranium extraction, and no generalizations can be made until a wider variety of compounds have been examined.

Extraction Of Uranium From Carbonate Solutions

It was noted in the previous report that, although the simple amines are not effective extractants from basic

solutions, reagents which are salts of strong bases, e.g., the quaternary ammonium compounds, might show uranium extractions comparable to sorption with strong base anion exchange resins. Results from a few early tests of the quaternary salts were somewhat encouraging and additional experiments were initiated for study of these compounds as possible uranium extractants from sodium carbonate liquors.

Since the quaternary ammonium compounds available for screening were in the form of the halide salt, a question arose as to the effect of this anion on the extraction of uranium. If the analogy to the ion exchange resin holds true, the affinity of the reagent for chloride ion could be sufficiently high to cause interference with the uranium extractions. On the other hand, this affinity would be lower for sulfate ions and better results might be obtained if the quaternary ammonium sulfate salts were used. In view of these considerations, screening tests were made with both the halide and the sulfate form of the reagents. The latter were prepared by contacting the organic solutions of the compounds with an aqueous sulfate solution, 1 M H_2SO_4 and 2 M Na_2SO_4, until no further halide could be detected in the aqueous phase. The organic portion was then ready for the evaluation studies.

The extraction behavior of the quaternary ammonium compounds was examined by subjecting each of the reagents in question to a simple series of extraction tests. In these tests, an alkaline uranium solution, U = 1 g/l, CO_3 = 0.5 M, pH = 10.7, was contacted in a separatory funnel with equal volumes of the following reagent-diluent mixtures: (a) halide salt of the reagent in chloroform, (b) sulfate salt of the reagent in chloroform, (c) halide salt of the reagent in benzene, and (d) sulfate salt of the reagent in benzene. After five minutes of vigorous shaking, the organic and aqueous phases were separated and the extractions measured by fluorometric determination of the uranium in each phase. Saturated solutions of the reagents were used in all cases where the limited solubility of the compound in the diluent prevented the use of 0.1 M solutions. The amount of reagent in the organic solvent was determined by evaporating a known volume to a constant weight. This method was also used to obtain an indication of the amount of reagent remaining in the solvent after contact with the aqueous liquor.

The screening test results are presented in Table 3. Significant extractions were obtained with three of the reagents tested and these were with chloroform as the diluent, i.e., Hyamine 10X, Hyamine 1622, and the cetyldimethylbenzyl compound. Extraction coefficients for these

Table 3

EXTRACTION OF URANIUM FROM CARBONATE SOLUTIONS

Compound	Halide Salt				Sulfate Salt						Phase Separation
	Chloroform		Benzene		Chloroform			Benzene			
	Init. Reagent Conc. g/l	E_a^o	Init. Reagent Conc. g/l	E_a^o	Reagent Conc. g/l Init.	Reagent Conc. g/l Final	E_a^o	Reagent Conc. g/l Init.	Reagent Conc. g/l Final	E_a^o	
Quaternary S	41.1	0.03	39.2	0.03	52.4	40.5	nil	1.7	2.2	nil	Halide Poor
Quaternary O	40	nil	39.6	0.03	47	43	0.17	1.7	2.9	nil	Poor
Quaternary C	35.5	nil	38.3	nil	47.9	18.2	< .001	1.3	1.8	nil	Fair
Hyamine 10X	44.7	2.9	1.4	0.03	52.5	54.1	4.5	1.8	0.9	< .001	Chloroform Poor
Hyamine 1622	42.8	2.2	0.4	nil	51.6	49.1	3.1	0.6	1.2	nil	Chloroform Poor
Trimethylphenyl-ammonium chloride	18.2	nil	0	nil	1.6	1.8	nil	0	1.1	nil	----
Cetyldimethyl-ethylammonium bromide	48.4	nil	19.5	nil	56.2	12.7	nil	---	3.8	nil	----
Cetyltrimethyl-ammonium bromide	38.2	0.26	1.7	0	42.0	12.1	0.01	1.7	2.9	nil	Poor
Cetyldimethyl-benzylammonium chloride	38.3	1.3	35.7	Third Phase	42.8	42.0	3.5	40.2	5.4	0.008	Benzene Fair
Cetylpyridinium chloride	34.2	0.002	5.5	0.001	43.8	6.8	nil	4.6	4.0	0.002	Poor
Laurylpyridinium chloride	27.8	nil	0.4	nil	31	2.6	nil	0.6	1.0	nil	Fair
Tributyllauryl-ammonium bromide	41.3	nil	23.1	nil	41.6	28.9	nil	23.3	19.0	nil	Good

Extraction Conditions: Aqueous = 1 g/l U, 5% Na_2CO_3, pH = 10.7.
Phase Ratio = 1 aqueous:1 organic.

reagents in the sulfate salt form were somewhat higher than those obtained with the chloride salts. Aqueous solubility losses of the chloride salts during extraction were not measured; by rough measurement the sulfate salts appeared to be almost completely retained in the chloroform phase.

In general, benzene was not a suitable diluent for these compounds. The first two reagents mentioned above, and many of the others tested, showed only limited miscibility with this solvent. The latter compound showed appreciably initial miscibility with benzene, but during the extraction tests was heavily distributed to the aqueous phase.

On the basis of the moderage encouragement given by these results, some further studies are planned to cover a wider variety of compounds and extraction conditions. It is apparent that reagents of this type must be tested, in the first instance, for diluent compatibility as well as for extraction power.

B. CHOICE OF DILUENT

The previous report described the importance of the diluent to be used in an extraction process and listed certain essential characteristics that it must possess. They are (1) immiscibility with the aqueous solution, (2) ability to dissolve the reagent and the extracted uranium complex, and (3) freedom from interfering interaction with the reagent. In addition, for a diluent to be of a practical value, it must also have a low vapor pressure and high flash point, low toxicity, low mutual solubility with the aqueous phase in contact, chemical stability in the system, suitable density and viscosity for ready separation from the aqueous phase, freedom from tendency toward emulsification, and it must be available in a quantity and at a cost commensurate with the intended operation.

The most versatile diluents reported were those of high aromaticity such as Amsco D-95 and Amsco G, with most of the work involving the former since it showed a somewhat wider compatibility with the various types of amines tested. Kerosene, although a desirable solvent in regard to physical properties and cost, gave acceptable extraction performances (absence of third phase formation) only with the long-chain symmetrical tertiary and certain

highly branched-chain secondary amines. It was indicated that the solvent power of kerosene might be improved by the addition of a small amount of a long-chain alcohol.

The diluent studies have now been extended to the more recent compounds and the most promising of the prior reagents have been investigated further under different conditions. As shown by the screening tests of Table 2, many of the newer compounds tested were highly branched-chain secondary amines of the type which had previously given indication of good compatibility with a kerosene diluent. Results below substantiate the earlier indications. Further studies of the addition of long-chain alcohols to the kerosene phase also establish that increased solvent power can be attained in this way. By adding only small amounts of alcohol to the kerosene phase, good performance could be achieved with essentially all of the recent as well as prior compounds which failed to perform in kerosene alone.

Amsco D-95 and Amsco G continued to show high solvent power for a wider variety of amines and, from general observations, phase disengagement appeared to be better with these diluents in borderline cases. The results in Section E show, however, that these diluents, particularly Amsco D-95, may have a disadvantage in addition to their higher initial cost. It has been observed that minor constituents in these diluents can react with the amines and render the reacted portion inert to the extraction process. Although it is possible that this effect might be reduced or eliminated as a natural part of a cyclic operation, it would, nevertheless, be a point of concern in establishing purchasing specifications for these solvents.

Miscibility Of Some Amine Sulfate And Bisulfate Salts With Various Diluents

When a solution of a free amine in an organic diluent is contacted with aqueous acidic sulfate solution (pH = 1-2) the amine reacts completely to form the sulfate and bisulfate salts. If the original amine concentration is greater than the miscibility level of these salts in the particular diluent employed, the excess will separate from the diluent as a solid precipitate or as a third liquid phase. This third phase lies between the diluent and aqueous layers, and although not specifically characterized it presumably contains diluent and water along with the amine salts.

As mentioned earlier, the tendency toward precipitation or third phase formation increases with increasing concentrations of sulfuric acid in the aqueous liquor, indicating lower miscibilities for the bisulfate than for the normal sulfate salts. The tendency appears to decrease, on the other hand, when extracted uranium or, to a lesser extent, iron is present in the organic phase. In a countercurrent extraction process, the liquor in the lower stages would be almost barren of uranium and only iron, in relatively low amounts, would be extracted at this point. Consequently, miscibility levels determined by contacting various amine-diluent solutions with "pure" acidic sulfate liquors (see below) should give reasonable approximations to those which would be experienced in actual operation on leach liquors of similar sulfate concentration and pH.

In former studies, direct measurements were made of the solubility (miscibility) of several pure alkylammonium normal sulfate salts in D-95. Recently additional measurements have been made with a wider variety of reagents in various diluents. Since the amine salts formed in a solvent extraction process would be a mixture of the normal sulfate and the bisulfate, a different procedure has been employed than that used in the past. Thus, instead of preparing the pure normal sulfate salt of a reagent and determining its solubility, the reagent salts were prepared by contacting solutions of the free amine with 0.5 M SO_4 solutions at various pH's with sufficient aqueous solution present to completely convert the free amine to salt form*. After equilibrium was attained, the precipitate was removed, if precipitation had occurred. The amount of reagent remaining in the filtrate, or in the clear top organic layer if three phases were present, was determined according to the methods outlined in Appendix B. The amount of amine (bisulfate-sulfate mixture) found represents the maximum retainable by the diluent upon contact with liquors of the particular composition (pH and sulfate concentration) employed in the experiment. Most of these liquors were in the range of composition expected in practice.

In tests where no precipitation (third phase) occurred, the miscibility of the salt mixtures (in terms of the free base) were reported (Table 4) to be equal to or greater than the original amine concentration. It was not considered

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*The amounts of bisulfate and sulfate in the salt mixture as a function of pH (0.5 M SO_4) are shown for two amines in Figures 1 and 2.

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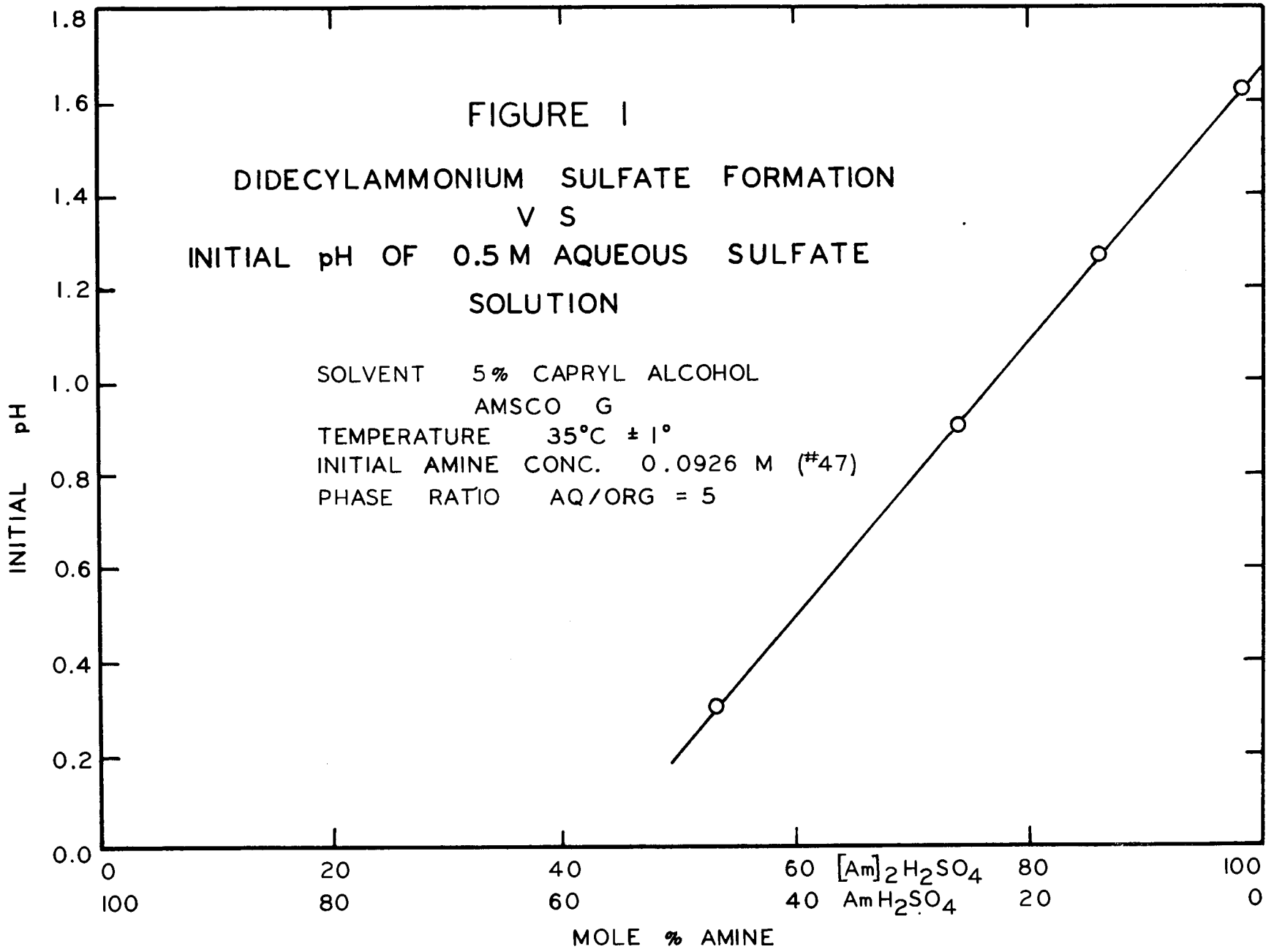

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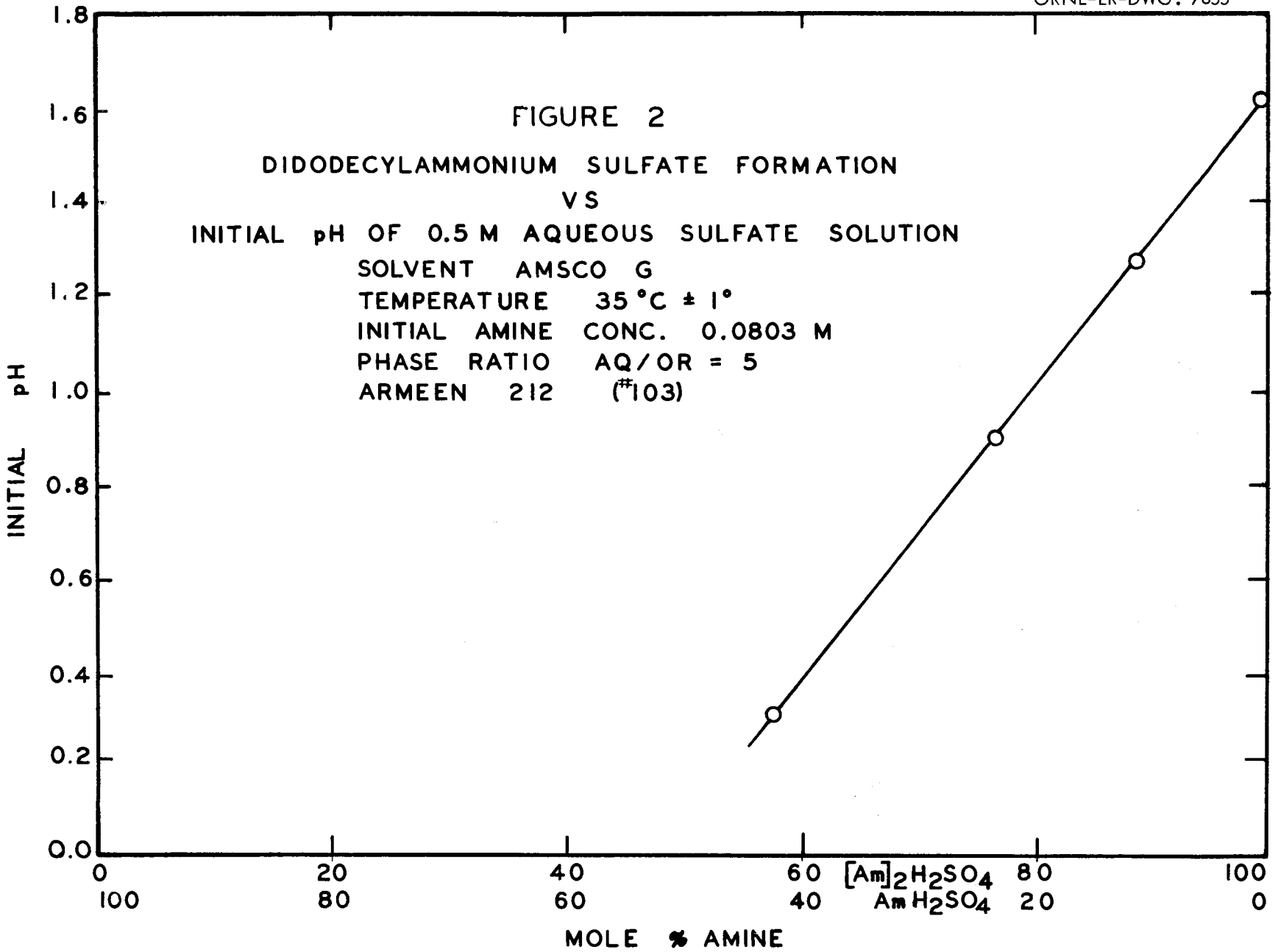

FIGURE 2

DIDODECYLAMMONIUM SULFATE FORMATION
VS
INITIAL pH OF 0.5 M AQUEOUS SULFATE SOLUTION

SOLVENT AMSCO G
TEMPERATURE 35 °C ± 1°
INITIAL AMINE CONC. 0.0803 M
PHASE RATIO AQ/OR = 5
ARMEEN 212 (#103)

Table 4

MISCIBILITY OF AMINE SULFATES WITH VARIOUS DILUENTS

Amine	Batch No.	Diluent*	Initial Aqueous pH	Temp.** °C	Miscibility of Amine (M)
Di-n-decyl	47	Amsco G	0.3	35	0.074
		"	1.0	20	0.043
		"	1.0	35	≥0.61
		Amsco G + 5% Cap. Alc.	0.3	35	≥0.093
		Solvesso 100	0.3	35	0.077
		Kerosene	1.0	35	<0.077
	47G	Kerosene + 5% Cap. Alc.	1.1	20	0.18
Dilauryl (Armeen 2-12)	103	Amsco G	0.3	20	0.023
		"	0.3	35	0.19
		"	1.0	20	0.057
	103E	"	1.3	35	≥0.32
	103	Amsco G + 5% Cap. Alc.	0.3	20	≥0.090
		" "	0.3	35	≥0.45
	103E	" "	1.3	35	≥0.45
	103	Amsco D-95	0.3	35	0.093
		Kerosene	0.3	35	0.012
		"	1.0	35	0.014
	103F	Kerosene + 5% Cap. Alc.	1.1	20	0.30
	103	" "	1.0	35	≥0.55
Di(2-butyloctyl)	198A	Kerosene	1.0	20	≥0.58
R&H 9D-178	193B	Kerosene	0.3	35	≥0.63
		"	1.0	0	≥0.11
		"	1.0	35	≥0.62
	193C	"	1.0	20	≥0.53
Di(Tridecyl P)	227A	Kerosene	1.1	20	≥0.87

Table 4 (Cont'd.)

MISCIBILITY OF AMINE SULFATES WITH VARIOUS DILUENTS

Amine	Batch No.	Diluent*	Initial Aqueous pH	Temp.** °C	Miscibility of Amine (M)
N-Benzyllauryl	199A	Kerosene + 5% Cap. Alc.	1.1	20	>0.1
N-Benzyl-1(3-ethylpentyl)-4-ethyloctyl	228A	Kerosene	1.1	20	≥1.00
Armeen 2S	151A	Amsco G	0.3	35	≥0.38
		"	1.0	20	≥0.27
		"	1.6	35	≥0.38
	151B	Amsco G	1.0	0-2	0.072
		Solvesso 100	1.0	0-2	0.080
		Kerosene	1.0	20	0.099
		Kerosene + 5% Cap. Alc.	1.0	20	≥0.20
		" "	1.0	35	≥0.29
Armeen 2T	152A	Amsco G	1.0	0-2	~0.046
		"	1.0	20	≥0.30
		"	0.3	35	≥0.35
	152B	"	1.6	35	≥0.35
		Solvesso 100	1.0	0-2	~0.046
		Kerosene	1.0	20	0.065
		"	1.0	35	0.086
	152C	"	1.0	20	<0.034
	152B	Kerosene + 5% Cap. Alc.	1.0	20	≥0.12
		" "	1.0	35	≥0.33
	152C	" "	1.0	20	<0.075
Tri-n-octyl	125H	Kerosene + 5% Cap. Alc.	1.0	20	≥0.59
Benzyldilauryl	200	Kerosene	1.1	20	≥0.98

*Capryl alcohol percentages are on a volume basis.
**Temperatures ± 1°C.

necessary to determine a more exact value in most cases since the majority of these concentrations were above those that would normally be employed in an extraction process.

In general, the conclusions to be drawn from the data in Table 4 are in agreement with those drawn from more limited experimentation described previously. That is, the solubility of the amine salts (1) improves with the addition of capryl alcohol to the diluent, (2) increases with temperature, (3) increases with branching and the presence of unsaturated groups, and (4) increases with the initial pH of the contacting aqueous phase (keeping temperature, diluent and sulfate concentration constant).

More specifically, it is shown that several of the long branched-chain secondary amines tested gave high miscibilities with kerosene, i.e, R&H 9D-178, di(2-butyloctyl)amine and di(Tridecyl P)amine. Similar results were also obtained with N-benzyl-1(3-ethylpentyl)-4-ethyloctyl- and benzyldilaurylamine. Total amine concentrations greater than 0.6 M were retained by the kerosene even when contacted by solutions of relatively low pH. With such a miscibility range, kerosene should be a suitable diluent for these reagents even in applications wherein the uranium concentration levels may demand a rather rich extracting phase. Other of the compounds which showed acceptable performance with kerosene in the screening tests (Table 2) have not been further examined in regard to their miscibility range. Further tests with these and other compounds are being made.

The saturated straight-chain secondary amines, di-n-decyl- and dilauryl-, continued to show good compatibilities with Amsco D-95 or Amsco G and very limited compatibility with kerosene. Better compatibilities with the Amsco diluents and good compatibility with kerosene were obtained by addition of 5 v % capryl alcohol.

Some samples of unsaturated straight-chain secondary amine mixtures, i.e., Armeen 2S and one batch of Armeen 2T (No. 152B), showed greater miscibilities with Amsco G and also kerosene than were shown by the saturated straight-chain secondary compounds. Again, the addition of alcohol to the hydrocarbon diluents appreciably increased the miscibility. A second batch of Armeen 2T (No. 152C) gave much poorer performance than the first batches tested. If compound mixtures of this type were to be used in practice, it would be necessary, apparently, to establish a quality specification.

Previous work has shown tri-n-octylamine to be limited in compatibility with kerosene, third phase formations (in contact with acidic sulfate liquors) being noted in several cases wherein the initial concentration of amine in kerosene was fairly low (0.1 M)*. As shown in Table 4, addition of 5% capryl alcohol to the kerosene allowed tri-n-octylamine to be retained in the kerosene at a concentration greater than 0.59 M when in contact with a 0.5 M sulfate solution, pH = 1, at 20°C.

Extractions Of Uranium From Synthetic Leach Liquors By Different Amines In Various Diluents

Typical extractions of uranium from a synthetic leach liquor by several amines in different diluents (benzene, Amsco D-95, Amsco G, kerosene, and kerosene modified with various amounts of alcohol) are shown in Table 5. Since the aqueous liquor contained an appreciable concentration of iron, the coefficients shown reflect differences in extraction selectivity by the compounds rather than extraction power alone. Differences in extractions with the same amine in different diluents also are not a direct function of diluent effect since the diluent may in turn have an influence on extraction selectivity. The results do serve to demonstrate, however, that effective extraction of uranium could be obtained from the liquors by each of the amine-diluent combinations tested. The magnitude of the coefficients in all cases should be sufficiently great for practical process application. Phase disengagements were also sufficiently rapid and clean.

Miscibility Of Amine Chloride And Nitrate Salts With Organic Diluents

In previous stripping studies it was noted (ORNL-1734, p. 87) that the chloride and nitrate salts of the straight

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*Third phase formation or lack of formation with tri-n-octylamine in kerosene (ordinarily 0.1 M) has been noted to be extremely sensitive to the aqueous pH in the region of pH = 1. In several extraction tests third phases were not noted at pH's slightly greater than 1, but were found to occur when the initial pH was reduced less than 0.1 unit - all other extraction conditions being equal.

Table 5

URANIUM EXTRACTIONS FROM SYNTHETIC LEACH LIQUOR

BY SEVERAL AMINES (0.1 M) IN DIFFERENT DILUENTS

Amine	Init. pH	Final pH	Benzene	Kerosene	Kerosene (2% v/v Capryl Alcohol)	Kerosene (3% v/v Capryl Alcohol)	Kerosene (5% v/v Capryl Alcohol)	Amsco D-95	Amsco G
Armeen 2T	0.85	----	60	---	---	--	60	45	45
	1.35	1.5	---	---	---	--	20	15	15
Armeen 2-12 (Cmpd. 103F)	0.85	0.98	40	---	---	--	30	30	25
R&H 9D-178	0.85	0.93	---	75	---	--	--	80	60
	1.4*	1.7	---	170	240	--	--	--	--
Tri-n-octyl (125H)	0.87	0.98	370	---	170	--	120	--	--
	1.35	1.5	>500	---	300	--	170	--	--
	1.8	2.2	>500	---	170	--	110	--	--
(116F)	1.8	2.1	500	---	---	--	90	120	70
16F27	0.9	1.0	---	125	---	--	---	--	--
Di(OxoDecyl)	0.9	0.98	---	---	40	--	---	--	--
Di(Tridecyl P)	0.9	1.0	---	40	---	70	---	--	--
N-benzyl-1(3-ethylpentyl)-4-ethyloctyl	0.9	1.0	---	>1500	---	--	---	--	--

Table 5 (Cont'd.)

URANIUM EXTRACTIONS FROM SYNTHETIC LEACH LIQUOR

BY SEVERAL AMINES (0.1 M) IN DIFFERENT DILUENTS

Amine	Init. pH	Final pH	Benzene	Kerosene	Kerosene (2% v/v Capryl Alcohol)	Kerosene (3% v/v Capryl Alcohol)	Kerosene (5% v/v Capryl Alcohol)	Amsco D-95	Amsco G
Bis(1-methyl-4-ethyloctyl	0.9	1.0	---	---	20	--	---	--	--
Benzyllauryl	0.9	0.98	---	---	--	35	---	--	--
Benzyldilauryl	0.9	0.98	---	---	--	50	---	--	--

Extraction Conditions: 0.1 M Amine, phase ratio $2^{aq}:1^{org}$.

Aqueous Composition: 1.25 g U/l, 0.1 M Fe^{+++}, 0.12 M Al^{+++}, 0.09 M F^{-}, 0.02 M $PO_4^{\equiv}$, 0.5 M $SO_4^{=}$.

*Same aqueous as above except U = 1 g/l.

chain secondary amines were less miscible with hydrocarbon diluents than the sulfate salts. In contrast to the long chain symmetrical tertiary and branched chain secondary amines, these compounds (even in Amsco D-95 diluent) gave emulsions during chloride and nitrate stripping which were apparently due to partial precipitation of the alkylammonium salts.

Further studies of the miscibility of amine chloride and nitrate salts in various diluents have not been made, per se. In process development work, however, successful chloride and/or nitrate stripping has been accomplished on R&H 9D-178, C&CCC 16F27, di(Tridecyl P) and N-benzyl-1(3-ethylpentyl)-4-ethyloctyl amines in kerosene, tri-n-octyl, di(Tridecyl P) and bis(1-methyl-4-ethyloctyl) amines in kerosene plus 2-3% capryl alcohol. It is expected that compounds generally similar in structure would be generally similar in performance.

C. DISTRIBUTION OF AMINES TO THE AQUEOUS PHASE

In addition to other essential properties, a useful extraction agent must be retained at effective concentration in the solvent phase without requiring excessive make-up. One of the important ways in which reagent may be lost is by distribution to the aqueous phase. Many such loss measurements were reported and discussed in detail in the last report[2]. Since that time these studies have been extended to other amines and conditions.

As before, the solubility loss was measured by a method which was basically equivalent to multicycle extraction, but which avoided the uncertainties of actual recycle operations and permitted a direct analysis for the amine concentration. Each loss measurement consisted of a series of batch equilibrations made simultaneously. A typical series used 5 ml samples of the organic with the volumes of the aqueous (presaturated with the diluent used in the organic phase) giving aqueous:organic phase ratios over the range from 5 to 100. The phases were mixed (mechanical agitation) in closed containers for 10 minutes at room temperature, then allowed to separate. A portion of the clear organic phase was treated with a two-fold excess of 0.1 N sodium hydroxide solution to strip out the extracted anions and to regenerate the free amine. (In the few tests in which uranium was present, sodium carbonate solutions were used as the strip to avoid any complications from uranium precipitation.) The organic solution was then

rinsed with an equal amount of water to remove any entrained base, and aliquots were titrated with perchloric acid in nonaqueous media (see Appendix B). Tests with methyldioctylamine (a compound with appreciable distribution to acid liquors) have shown no measurable loss of amine to the basic strip or to the water rinse.

The results from these recent experiments are in agreement with previous results in that the loss curve obtained by plotting each final amine concentration against the corresponding phase ratio was a straight line (cf. page 46, ORNL-1734). Some of the amines showed, as before, a rapid rate of loss at low aqueous:organic ratios followed by a much slower rate at higher ratios. The best explanation for this continues to be that the principal amine contains a significant admixture of other titratable bases which are more water-soluble, perhaps because of low molecular weight. In view of the above, the solubility loss rates recently determined and summarized in Table 6 are based on the same assumptions as before - (1) that some of the amine samples contained a relatively soluble fraction that was more readily lost than the principal amine and (2) that the characteristic loss curve for an absolutely pure amine should be a straight line. Accordingly, the next-to-last column in Table 6 presents the fraction readily lost expressed as percent of the initial quantity of amine, and the last column presents the subsequent steady-state loss rate expressed as parts of amine per million parts of aqueous raffinate. Even though the validity of the two suppositions still has not been rigorously proved, the data give a concise empirical summary of the total losses actually measured.

The solubility loss measurements listed in Table 6 include tests of new compounds obtained since the last report, tests of new batches of compounds nominally the same as reagents previously reported and also some experiments with the same compound batches examined previously but under somewhat different conditions. In instances where nearly exact comparisons of the same compound batches were possible, the recent measurements were in excellent agreement with those reported earlier in Table 7, ORNL-1734. Also in agreement are general observations of factors influencing the solubility loss. For example: under a given set of conditions, loss of amine into sulfate solution is less at higher pH; the loss into a given solution can be dependent on the diluent, a greater loss usually being incurred from kerosene than from benzene; and, for a specific type of amine, the losses of the individual amines to a given solution are primarily related to their molecular weights. In addition to these relation-

Table 6

LOSS OF AMINE TO AQUEOUS PHASE

Amine	Organic Phase: Compound No.	Organic Phase: Neut. Eq.[c]	Organic Phase: Init. Conc. M	Organic Phase: Diluent[b]	Aqueous Phase[a]: Solute	Aqueous Phase[a]: Conc. M	Aqueous Phase[a]: pH	Loss of Amine: Fraction Readily Lost, % of Init.	Loss of Amine: Steady-State Loss ppm/aq
Primary									
Primene JM-T	6A	363	0.105	Amsco G	SO_4	0.9	0.18	12	45
	6B	297	0.105	Amsco G	SO_4	0.9	0.18	13	105
Primene JM-R	6C	313	0.102	Amsco G	SO_4	0.9	0.18	14	78
			0.109	Kerosene	SO_4 + PO_4	1.2 0.3	0.1-0.2	26	52
			0.106	Amsco G	SO_4 + PO_4	1.2 0.3	0.1-0.2	13	58
			0.202	Kerosene	HNO_3	1		9	70
			0.202	Kerosene	HNO_3	2		7	70
			0.202	Kerosene	HNO_3 + $NaNO_3$	0.1 0.9		4	80
Secondary									
Di(2-ethylhexyl)	26A	248	0.1	Amsco G	Syn. Leach Liquor			--	1.5×10^3
Didecyl	47F	309	0.099	Amsco G	Syn. Leach Liquor			< 1	6

Table 6 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

Amine	Organic Phase: Compound No.	Neut. Eq.[c]	Init. Conc. M	Diluent[b]	Aqueous Phase[a]: Solute	Conc. M	pH	Loss of Amine: Fraction Readily Lost, % of Init.	Steady-State Loss ppm/aq
Di(OxoDecyl)	197A	323	0.0928	Kerosene + 5% Cap.Alc.	Syn. Leach Liquor			33	23
Armeen 2-12	103F	354	0.0927	Amsco G + 5% Cap.Alc.	H_2SO_4	0.2		< 1	< 5
			0.100	Kerosene + 5% Cap.Alc.	Syn. Leach Liquor			< 1	13
	103E	382	0.097	Amsco G	Syn. Leach Liquor			2.5	< 5
	123		0.068	Amsco G	Syn. Leach Liquor			< 1	< 5
15F53	119B	274	0.1	Amsco G	Syn. Leach Liquor			30	$2x10^3$
N-(2-ethylhexyl)-1-isobutyl-3,5-dimethylhexyl	225A	298	0.100	Kerosene	Syn. Leach Liquor			16	170
Bis(1-methyl-4-ethyloctyl)	229B	325	0.100	Kerosene	Syn. Leach Liquor			5	< 5
Di(2-butyloctyl)	198A	355	0.100	Kerosene	Syn. Leach Liquor			2.5	< 5

Table 6 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

Amine	Organic Phase: Compound No.	Neut. Eq.[c]	Init. Conc. M	Diluent[b]	Aqueous Phase[a]: Solute	Conc. M	pH	Loss of Amine: Fraction Readily Lost, % of Init.	Steady-State Loss ppm/aq
16F27	30B	360	0.099	Kerosene	Syn. Leach Liquor			24	14[d]
Di(Tridecyl P)	227A	371	0.099	Kerosene	Syn. Leach Liquor			10	5
R&H 9D-178	193B	378	0.104	Kerosene	Syn. Leach Liquor			3	24
	193B		0.099	Amsco G	"	"	"	2.5	10
	193C	371	0.103	Kerosene	"	"	"	6.7	31
	193C		0.100	Kerosene + 5% Cap.Alc.	"	"	"	6.4	21
	193C		0.103	Benzene	"	"	"	2.4	11
	193D	371	0.099	Kerosene	"	"	"	10	16
Armeen 2S	151B	582	0.104	Kerosene	Syn. Leach Liquor			No value (Emulsions)	
Armeen 2T	152B	570	0.0950	Kerosene	Syn. Leach Liquor			No value (Emulsions)	
			0.0961	Kerosene + 5% Cap.Alc.	"	"	"	< 1	< 5
	152C	488		Kerosene + 5% Cap.Alc.	"	"	"	No Value (Emulsions)	

Table 6 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

Amine	Organic Phase: Compound No.	Neut. Eq.[c]	Init. Conc. M	Diluent[b]	Aqueous Phase[a]: Solute	Conc. M	pH	Loss of Amine: Fraction Readily Lost, % of Init.	Steady-State Loss ppm/aq
Armeen 2T				Benzene	Syn. Leach Liquor			No Value (Emulsions)	
N-benzyl-1(3-ethylpentyl)-4-ethyloctyl		348	0.099	Kerosene	Syn. Leach Liquor			< 1	< 5
Tertiary									
Methyldi-n-octyl	133A	303	0.100	Amsco G	Syn. Leach Liquor			< 1	360
			0.0848	Amsco G + 5% Cap.Alc.	" " "			< 1	185
			0.0864	Benzene	" " "			< 1	155
			0.0864	Benzene	Syn. Leach Liquor + 0.004 M U		0.78	< 1	91
			0.100	Benzene	Syn. Leach Liquor + 0.004 M V		0.77	< 1	164
			0.100	Benzene	Syn. Leach Liquor + 0.004 M U + 0.004 M V		0.82	< 1	85

Table 6 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

Organic Phase					Aqueous Phase[a]			Loss of Amine	
Amine	Compound No.	Neut. Eq.[c]	Init. Conc. M	Diluent[b]	Solute	Conc. M	pH	Fraction Readily Lost, % of Init.	Steady-State Loss ppm/aq
Tri-n-octyl	116F	372	0.0905	Amsco G	Syn. Leach Liquor			9	15
	116F		0.084	D-95	Leach Zone Liquor			5	19
Tri-n-octyl Prewashed with H_2SO_4	116F	372	0.087	D-95	Leach Zone Liquor			< 1	26
Tri-n-octyl	125G	402	0.100	Benzene	Syn. Leach Liquor			2	< 5
	125H	350	0.101	Kerosene	" " "			3 Phases	
			0.101	Kerosene + 5% Cap. Alc.	" " "			< 1	17
			0.101	Kerosene	3 g U/l; 0.4 g V/l; 0.5 M SO_4; pH = 1.6			< 1	< 5
			0.0996	Kerosene	0.022 g U/l; 0.17 g V/l; 0.5 M SO_4, pH = 1.95			< 1	< 5
Dibutyllauryl	100A	292	0.10	Amsco G	Syn. Leach Liquor			< 1	87
Di(Nonyl B)-butyl	232A	320	0.098	Kerosene + 2% Cap.Alc.	Syn. Leach Liquor			4	480[f]

Table 6 (Cont'd.)

LOSS OF AMINE TO AQUEOUS PHASE

Amine	Organic Phase: Compound No.	Neut. Eq.[c]	Init. Conc. M	Diluent[b]	Aqueous Phase[a]: Solute	Conc. M	pH	Loss of Amine: Fraction Readily Lost, % of Init.	Steady-State Loss ppm/aq
Dihexyl(Tridecyl B)	164B	368	0.104	Kerosene	Syn. Leach Liquor			28[e]	< 5[e]
Dihexyl(Tridecyl B)	164B		0.098	Kerosene + 2% Cap.Alc.	Syn. Leach Liquor			22	< 5
Benzyldilauryl	200A	444	0.10	Kerosene	Syn. Leach Liquor			15[e]	50[e]

Tests were made at room temperature.

	Ion:	U	Fe	Al	Ca	F	PO_4	SO_4	pH
a) Composition of synthetic leach liquor:	g/l:		5.8	3.3		1.7	2.0	50	0.7-0.8
Leach Zone liquor:	g/l:	0.05	0.2	1.5	0.4	0.2	4.1	20	1.1

b) Capryl alcohol percentages based on volumes.

c) Titration values determined at this laboratory.

d) The new batch of C&CCC 16F27 (Cmpd. 30B) showed a lower steady-state loss than the previous batch tested (Table 7, ORNL-1734). Better extractions were also shown by the newer sample as described in Section A.

e) Tentative values due to the presence of a slight third phase. For the benzyldilaurylamine such a formation was unexpected in view of the miscibility measurements described in Table 4 and further studies are being made.

f) From tests at phase ratios up to $50^{a}:1^{o}$.

ships the recent tests have shown that the distribution of amine to the aqueous phase is decreased by the presence of a long-chain alcohol, and also by the presence of uranium. In the cases tested with capryl alcohol (R&H 9D-178 and methyldioctylamine in Table 6), addition of only a small amount to the amine-diluent phase tended to reduce the distribution loss. Addition of 1 g uranium/liter to the "synthetic leach liquor" considerably decreased the loss of methyldioctylamine from benzene solution.

With the exception of N-(2-ethylhexyl)-1-isobutyl-3,5-dimethylhexylamine and di(Nonyl B)butylamine, all of the newer amines examined thus far showed fairly low steady-state solubility losses. Very low losses ($<$5 ppm) were shown by di(2-butyloctyl)amine, di(Tridecyl P)amine, N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine, bis(1-methyl-4-ethyloctyl)amine, dihexyl(Tridecyl B)amine and Armeen 2T. Losses of R&H 9D-178, C&CCC 16F27, and di(OxoDecyl)-amine were significant but not sufficient to prevent their use in process application. Several of the more favorable recent compounds tested, such as Primene JMR, R&H 9D-178, di(Tridecyl P), bis(1-methyl-4-ethyloctyl), C&CCC 16F27, dihexyl(Tridecyl B), and di(OxoDecyl) amines, showed a significant initial solubility loss. In the first four cases the extent of this loss was of a reasonable order and, in process application, would be reflected as a moderate increase in the purchase price of the amine. With the latter three, however, the initial loss was very high. If these materials are representative of those expected from commercial production, a very low comparative selling price would be required for them to be competitive with the more promising of the other reagents tested.

As a matter of experimental practice at this laboratory, those amines with a measurable initial solubility loss are thoroughly scrubbed with dilute sulfuric acid prior to their use in laboratory development or pilot plant studies. The readily soluble fraction is thus removed and the test results are directly attributable to the major constituents.

D. SELECTIVITY FOR URANIUM

With Respect To Titanium

In tests reported earlier, the selectivity properties of several amines were examined by measuring the individual extractions of certain metal ions from sulfate solution

(Table 4, ORNL-1734). Similar tests have subsequently been made with titanium(IV), another metal ion sometimes encountered in sulfate leach liquors.

The variations in titanium extractions with amine types, Table 7, were similar to those obtained with other quadrivalent metals, in that more titanium was extracted by the primary amine than by the secondary and tertiary amines, and somewhat more was extracted by the straight-chain secondary than by the highly branched secondary or the tertiary amine. (Di-2-ethylhexylamine and di(Tridecyl P)amine, with branching at the second and third carbon away from the nitrogen, respectively, were more similar to the straight chain dilaurylamine than to the highly branched C&CCC 15F53, i.e., di(1-isobutylisopentyl)amine.) However, the amount of titanium extracted by each type of amine was much lower than was the extraction of zirconium (ORNL-1734, p. 37), which is the metal most closely related to titanium of those previously tested. The extraction coefficient for titanium increased with increasing pH and decreased with increasing sulfate concentration as had also been found with most of the metal ions previously tested. In comparison with uranium, titanium extraction by the tertiary and secondary amines was very low, and should not be significant in uranium processing.

The results also suggest that under suitable conditions the primary amine (and perhaps the less branched secondary amines) could be useful for recovery of titanium from sulfate liquors.

Erratum

High coefficients for Ce(IV) from sulfate solutions with 0.1 M tri-n-decylamine in Amsco D-95 were mistakenly reported in ORNL-1734, p. 37. The coefficients at pH of 0.3, 0.9 and 1.8 should have been 0.2, 0.4 and 0.4, respectively. Even these coefficients may be higher than actual since the amine used in the tests was from a batch of questionable purity.

Table 7

EXTRACTION OF TITANIUM(IV) BY AMINES

Amine	Diluent	Phase Ratio a/o	Head Aqueous Solution Ti (g/l)	SO_4 (M)	pH	E_a^o
C&CCC 21F81	Kerosene	1	0.25	0.5	0.3	>50
	"	1	"	"	0.9	>50
	"	1	"	"	1.4	>50
	Amsco D-95	2	"	1.0	0.2	10*
	"	2	"	"	0.9	12*
Dilauryl	Amsco D-95	1	0.57	0.5	0.3	pptn.**
	"	1	"	0.5	1.0	4
	Amsco D-95	2	0.25	1.0	0.2	0.02
	+ 10 v % Capryl Alc.	2	"	1.0	0.9	0.08
Di(2-ethyl-hexyl)	Amsco D-95	1	0.57	0.5	0.3	0.08
	"	1	"	0.5	1.0	1.9
	"	2	0.25	1.0	0.2	0.04
	"	2	"	1.0	0.9	0.2
Di(Tridecyl P) (Scrubbed)***	Kerosene	1	0.25	0.5	0.3	0.5
	"	1	"	"	0.9	2.3
	"	1	"	"	1.4	3.8
R&H 9D-178 (Scrubbed)***	Kerosene	1	0.25	0.5	0.3	0.3
	"	1	"	"	0.9	0.5
	"	1	"	"	1.4	1.1
C&CCC 15F53	Amsco D-95	1	0.57	0.5	0.3	0.04
	"	1	"	"	1.0	0.2
Tri-n-octyl	Kerosene	1	0.25	0.5	0.3	0.06
	+ 5 v %	1	"	"	0.9	0.04
	Capryl Alc.	1	"	"	1.4	0.08

Extraction Conditions: 0.1 M amine, 10 min contact time at 25°C.

*Coefficients may be significantly affected by loading of the reagent in the organic phase.

**A white precipitate formed - presumably the sulfate or bisulfate salt of the amine.

***Reagents were scrubbed with large volumes of acidic sulfate solution to remove readily soluble fraction prior to use.

With Respect To Iron And Some Other Elements

The selectivity properties of the newer amine reagents have not been tested in regard to extraction of individual metal ions such as described above for titanium and described previously for other metals (p. 34, ORNL-1734). However, several of the more promising reagents have been compared, in process development studies, with respect to their extractions from ore leach liquors. Observations made from these studies (to be described in detail in a subsequent report) are itemized below. The general relationships between selectivity properties and compound structures serve to substantiate and expand the observations made on the basis of earlier data. Thus,

1) Of the compound types examined, the symmetrical tertiary amines, e.g., tri-n-octyl-, tri-n-decyl-, and trilauryl-, have continued to show the greatest selectivity for uranium with respect to iron and most of the tetravalent metals. Except for molybdenum (which is highly extracted by all of the amines) only small extractions have been obtained with other metals tested.

2) The highly branched secondary amines, such as C&CCC 16F27 and C&CCC 15F53, i.e., bis(1-isobutyl-3,5-dimethylhexyl) and di(1-isobutylisopentyl) amines, have somewhat lower selectivities than the symmetrical tertiary amines in regard to iron and certain tetravalent metals, e.g., thorium. Dependent upon the extraction conditions, particularly the aqueous pH, their selectivity properties may be equivalent or even superior to the symmetrical tertiaries in regard to other metals such as Ce(IV), Zr, and U(IV). In both of the compounds mentioned, branched alkyl groups are attached to the nitrogen through a secondary carbon. With a similar but less branched compound, bis(1-methyl-4-ethyloctyl)amine, the comparative selectivity properties were somewhat poorer, but still were better than those for secondary amines described under (4) below.

3) Only limited testing has been given the unsymmetrical tertiary amines. On the basis of available data, the longer chain compounds of this type, e.g., dilaurylhexyl- and dihexyllaurylamines, appear to have selectivity properties similar to those described for the amines under (1) and (2) above. The methyldialkylamines such as methyldidecylamine appear to be somewhat less selective with respect to iron. However, the samples of these compounds used in the tests were of questionable "purity level" and further studies are being made with reliable samples.

4) Secondary amines with moderate branching, branching at a distance from the nitrogen or no branching at all, are less selective for uranium than the highly branched secondary amines described under (2) above. This group is meant to include di(2-butyloctyl)amine, R&H 9D-178, di(Tridecyl P)amine, dilaurylamine, etc. Significant differences in properties within these compounds have been noted, e.g., the more highly branched 9D-178 amine (nitrogen attached to one tertiary and one primary carbon) extracts less iron than di(Tridecyl P)- or dilaurylamine, but the order of differences is smaller than those between, for example, these compounds as a group and the symmetrical tertiary amines as a group. The selectivity properties of all of the secondary amines mentioned are, however, completely acceptable for process application. Small but significant quantities of iron are extracted in the lower stages of a countercurrent operation, but the coefficients for iron and uranium are such that most of the iron is replaced by uranium in the upper stages. Tetravalent metals are also extracted to some extent by the less branched secondary amines but again the relative coefficients are such that good separations of uranium are permitted. Studies with uranium-thorium sulfate liquors, for example, have shown good uranium separations (see below).

5) The benzyl-alkyl amines (see Section A) have been only partially evaluated in respect to their uranium selectivity. The N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine, which gave extraordinarily high uranium extraction coefficients, has not shown correspondingly greater coefficients for iron. In process application where advantage can be taken of these coefficient differences by loading the organic phase, this reagent should prove to be a very selective extractant as well as a very efficient one.

6) The primary amines have shown very poor selectivity in regard to iron(III). They do not, however, extract iron(II) and could apparently be used as extractants for most sulfate leach liquors if the iron were reduced. Tetravalent metals, particularly thorium, are effectively extracted from sulfate solutions by the primary amines. A process has been proposed in which these reagents are used to extract thorium from sulfuric acid digests of monazite sand.[3]

7) The selectivity properties of the amines have varied noticeably with variations in the diluent. With several amines tested, better selectivities have been obtained using kerosene modified with alcohol than when

using kerosene alone. Selectivities have also been somewhat better in several cases with Amsco D-95 diluent as compared to kerosene.

With Respect To Thorium

Recently large deposits of uranium ores containing appreciable amounts of thorium have been discovered in Canada. If such ores were processed with sulfuric acid, amine extractants would appear to be promising reagents for solvent recovery of uranium from the liquors produced. A clean separation of uranium from the thorium could be achieved with tertiary amines, since these compounds have little or no tendency to extract thorium. The secondary amines would be less selective, but satisfactory thorium decontamination should be achieved if the operation were conducted so that the organic phase was loaded to near saturation with uranium. (Scrubbing the organic phase with dilute sulfuric acid prior to stripping could also be considered to increase product purity.) The more selective highly branched secondary amines would be more effective in respect to uranium-thorium separation than the straight chain or less branched secondary amines.

Table 8 shows the uranium and thorium distribution between the aqueous and organic phases when solutions of tri-n-octylamine and R&H Amine 9D-178 in kerosene (2 v % capryl alcohol) were contacted with a synthetic sulfate liquor at pH 0.9 and 1.4. In all cases thorium extraction by 0.1 M tri-n-octylamine was below the limit of analytical measurement. Appreciable amounts of thorium were extracted by 0.1 M R&H Amine 9D-178 in tests where the organic phase was at a low uranium level, but with increased uranium loading the amount of extracted thorium was decreased to only 4-5% of that of the uranium. It should be possible to limit thorium contamination still further in countercurrent operation where uranium loading of the organic phase could be even greater. There was little difference in the thorium decontamination factors observed when the pH was increased from 0.9 to 1.4.

If desired, it should be possible to recover thorium from the raffinate of the uranium recovery operation using a primary amine, and perhaps certain secondary amines if the conditions were appropriately adjusted.

Table 8

URANIUM-THORIUM EXTRACTION BY R&H AMINE 9D-178 AND TRI-n-OCTYLAMINE FROM 0.5 M SULFATE SOLUTIONS

Amine	Phase Ratio a/o	pH		Analysis (g/l)				Extraction Coefficient		Thorium Decontamination Factor*
				Aqueous		Organic				
		Init.	Final	U	Th	U	Th	U	Th	
R&H 9D-178	3	0.90	1.0	0.05	0.79	3.0	0.49	60	0.6	6
	6	0.90	0.94	0.3	0.89	3.2	0.15	11	0.17	21
	3	1.40	1.53	0.033	0.77	2.9	0.68	90	0.9	4
	6	1.40	1.42	0.31	0.94	3.6	0.16	12	0.17	22
Tri-n-octyl	3	0.90	1.0	0.008	0.84	2.4	<0.03	300	<0.05	>80
	6	0.90	0.93	0.10	0.89	5.1	<0.03	50	<0.05	>170
	3	1.40	1.50	0.004	0.88	2.7	<0.03	500	<0.05	>80
	6	1.40	1.45	0.10	0.96	5.2	<0.03	50	<0.05	>170

$$* \frac{\text{Th/U in head liquor}}{\text{Th/U in organic}}$$

Extraction Conditions:
- Head aqueous: 1 g U/l, 1 g Th/l, 0.5 M SO_4, indicated pH.
- Organic: 0.1 M amine in 98% kerosene - 2 v % capryl alcohol.
- Contact Time: 2 min.
- Temperature: R.T.

E. STABILITY OF AMINES

Amines can be oxidized by strong oxidizing agents[5], the extent of the reaction and the nature of the products depending on the type of oxidizing agent and the class of amine as well as on the reaction conditions. When used as extraction agents the amines can be exposed to the oxidizing action of dissolved air and of such metals as are present in their higher oxidation states; hence, several series of tests were made to determine whether amine loss by chemical reaction might be important under various conditions of process use. Laboratory-scale tests with a tertiary and three secondary amines showed no important loss in titratable base at ambient temperatures (23-28°C) under expected process conditions. More reaction was found in tests made at higher temperatures, under strong illumination, or at very long extraction contact times, the loss rate becoming severe under some extreme conditions.

Table 9 shows the results of tests (50-250 cycles) made under the type of conditions expected to be encountered in process use*. For convenience, the decrease in amine concentration is reported as parts of amine lost per million parts of raffinate passed as well as in molarity units, so that the magnitude of the total loss measured can be compared with the loss rates by distribution to and by entrainment in the raffinate. The losses measured, of course, include any loss by distribution to the raffinates (see Section C), which in these tests may have been a major fraction of the total. Although the losses found are so small that the differences among them are not very significant, it may be noted that they do indicate increased loss in the presence of vanadium(V).

At intervals throughout the cyclic extractions, stripped samples of the organic phases were loaded with uranium under standardized conditions. The resulting mole ratios of extracted uranium to amine were in the range usually found in such tests. Similarly, extraction coefficients estimated from the strip solutions and the raffinates were found to be fairly uniform.

*The conditions of the tests were intentionally such that more vanadium was extracted than would be expected in actual process use. Hence, the extraction tests involving vanadium were probably somewhat more severe than would be typical in respect to oxidation by vanadium.

Table 9

STABILITY OF AMINES IN CYCLIC EXTRACTIONS

Room Temperature

Amine (0.1 M)	Diluent[a]	Aqueous Phase[b]	Extrn. Time/ Cycle[c] (min.)	Cycles	Amine Loss (Parts Per Million Parts Raffinate)	Amine Loss Total Decrease in Conc. Δ M
Tri-n-octyl (Cmpd. 125H)	Kerosene	U-V Sulfate Soln.	5	200	23	0.013
	"	" " "	"	250	22	.016
	"	Syn. U-V Liq.	"	200	20	.012
	"	" " "	"	250	22	.016
	Ker. + Alc.	Syn. U Liq.	15	50	< 5	.000
	" "	Syn. U-V Liq.	"	"	10	.001
Di(2-butyloctyl) (Cmpd. 198)	Kerosene	U-V Sulfate Soln.	5	200	5	0.003
	"	Syn. U-V Liq.	"	"	5	.002
Di(Tridecyl P) (Cmpd. 227A)	Kerosene	Syn. U Liq.	15	50	< 5	0.000
	"	Syn. U-V Liq.	"	"	10	.001
R&H 9D-178 (Cmpd. 193C)	Kerosene	Syn. U Liq.	15	50	20	0.003
	"	Syn. U-V Liq.	"	"	30	.004
	Ker. + Alc.	Syn. U Liq.	"	"	10	.001
	" "	Syn. U-V Liq.	"	"	30	.003

Table 9 (Cont'd.)

STABILITY OF AMINES IN CYCLIC EXTRACTIONS

Room Temperature

Notes:

a). Alcohol where indicated was capryl alcohol, 3 v %.

b) Each solution was 0.5 M in sulfate, initial pH 1.6 - 1.7, final pH ~2. Each contained 2-4 g U/l, and the "U-V Sulfate Solution" and "Synthetic U-V Liquor" contained 0.5-2 g V(V)/l. The "synthetic liquors" also contained iron(III), aluminum, manganese(II), molybdenum(VI), copper(II), and fluoride.

c) Extraction phase ratio was 1:1. Each cycle was completed by stripping with 6% sodium carbonate solution at $1^{a}:2^{o}$ for 5-10 minutes.

Amine	Molar Ratio, Measured Amine/(U)org			
	Head	20	50	200 Cycles
Di(2-butyloctyl)	6.2		6.1	5.6
Trioctyl	4.7		5.0	4.6
"	5.2	4.7	4.8	
R&H 9D-178	6.6	7.6	7.4	
" (with Alc.)	6.6	6.9	7.1	
Di(Tridecyl P)	6.1	-	6.6	

The loss rates given in Table 9 were measured only in terms of the total titratable base present in the organic phase. This leaves some uncertainty with respect to trioctylamine in these cyclic extractions, for subsequent tests (described below) have shown a very slow conversion of trioctylamine to other (unidentified) bases which can be distinguished by differential but not by simple titration. Thus, it is conceivable that a higher proportion of the trioctylamine than indicated in the 200-250 cycle tests (Table 9) may have undergone some kind of a reaction, and that the observed average loss rate of 20-25 ppm was actually the distribution loss rate of the basic product. At the same time it may be noted that, if such a conversion did occur to any great extent, the unknown product must have been a fairly strong and stable uranium extractant, since the measured uranium loading ratios and extraction coefficients were in line with the amine titrations.

The actual importance of each loss rate found depends on the corresponding uranium production level and hence on the uranium assay of the pregnant leach liquor. For a typical example of 1 g U/l, 20 ppm loss is equivalent to loss of one pound of amine per 60 pounds of U_3O_8 produced, or less than 2¢/lb U_3O_8 for an amine priced at not over a dollar per pound.

When contact time was greatly prolonged, in cyclic extractions from the same type of synthetic uranium-vanadium liquor as included in the preceding tests, the loss of amine per volume of liquor passed was an order of magnitude higher. Here the extraction conditions were the same as in Table 9 except that in each cycle the extraction

Amine	Loss: % Lost in 240 Hr Extr. 105 Hr Strip.	Loss: ppm/ Raffinate at 16 Hr Extr. Residence/ Cycle	Loss: Calcd. ppm/ Raffinate at 30 Min Extr. Residence/ Cycle
Di(2-butyloctyl) in kerosene	2	55	2
R&H 9D-178 in kerosene	9	230	7
R&H 9D-178 in kerosene + 3% capryl alcohol	6	160	5

contact time was 16 hours and the stripping contact time was 7 hours, and the tests were carried through 15 cycles for a total of 240 hours extraction contact time. (Since the increased contact time should not increase the loss by simple distribution to the aqueous phase, the losses found are ascribed essentially entirely to chemical reaction.) The tests with R&H 9D-178 indicate that capryl alcohol in the kerosene gave some protection against the loss of the amine.

When the temperature was raised from room temperature (23-28°) to 45°C, the loss of di(2-butyloctyl)amine/kerosene was greater under nearly the same extraction conditions

Liquor	Amine Loss at 45°C: % Lost in 250 Hr Extr. 65 Hr Strip.	Amine Loss at 45°C: ppm/ Raffinate at 30 Hr Extr. Residence/ Cycle	Amine Loss at 45°C: Calcd. ppm/ Raffinate at 30 Min Extr. Residence/ Cycle
Syn. U-V Liq.	11	~500	~8
Syn. U Liq.	1	< 100	< 2
0.5 M SO_4, pH 1.6	< 1	< 100	< 2

(with 16 to 40 hours extraction contact time per cycle, average ~30). Because these tests were carried through only 8 cycles, the loss rate as based on the raffinate volume cannot be calculated as closely as in the preceding tests. Thus, the losses listed as "<100" in the absence of vanadium may have been similar to or even less than the 55 ppm loss rate found in the presence of vanadium at room temperature. The increased loss with increase of temperature in the presence of vanadium was marked.

Qualitative and semiquantitative tests of benzene solutions of trioctylamine, didecylamine, and Armeen 2-12 in prolonged contact with acidic vanadium sulfate solutions generally showed little loss in amine titer at room temperature, but considerable loss at 45-50°C.

Photochemical Reaction. Some decomposition of amines under strong illumination was observed qualitatively during synthesis and purification of reagents. A few quantitative tests made with solutions of trioctylamine in benzene (0.05 M) under oxygen, exposed to various levels of illumination for two weeks at room temperature and at 40°C, confirmed the occurrence of photochemical reaction and also indicated that it would be negligible under the conditions probable in normal use. In the tests under strong illumination a considerable fraction of the amine

Illumination	Temp.	Decrease in Conc., Δ M, in two weeks	
		Unwashed	Washed
None	~25°C	0.001	0.001
"	40°	.000	---
Normal	~25°	.003	.004
Strong (heat lamp)	~30°	.012	.014
" (UV lamp)	~30°	.009	.011

(Initial concentration = 0.05 M)

reacted to form non-basic material. A smaller fraction, although still basic, had become water-soluble and was

lost to a water wash. (This might result from, e.g., dealkylation to form amines of lower molecular weight or from oxidation to the more water-soluble amine oxide.) The sample subjected to higher temperature without light did not decrease in basic titer. (This sample was not washed to test for water-soluble products.)

Effect of Prolonged Aging. Several dilute solutions (~0.1 M) of amines in benzene or kerosene which had been analyzed for primary-secondary-tertiary content when freshly prepared were checked again after about six months. The solutions had been stored in contact with air inside stoppered flasks, under normal laboratory illumination. The analyses, Table 10, show essentially no change in the straight chain didecylamine, small but measurable degradation of the branched chain di(2-butyloctyl)amine, and large changes in the two tertiary amines. On the other hand, similar tests of the undiluted tri-n-octylamine stock showed no measurable deterioration in eight months.

It must be noted that the molarities of the primary, secondary, and tertiary components were calculated from differential titrations using the assumption that these three classes of simple amines included all the titratable bases present. If other bases (as perhaps amine oxides, hydroxylamines, hydrazines) were formed, the calculations would be affected in an unknown manner. Hence, the molarities as listed must be considered provisional, and used primarily as qualitative evidence that degradation did or did not occur.

The dilute tri-n-octylamine solution was also tested by uranium loading after it had aged from October to February. The extracted uranium reached a mole ratio, amine:U, of 5.9, based on the total titratable amine content of 0.093 M, in good agreement with the ratios usually reached in such tests. As was indicated above with respect to the tests in Table 9, the uranium loading capacity gives a useful (although not very sensitive) corroboration that the unknown reaction products did not include a large amount of any base very much different in nature from the simple amines.

It was also noted above that this degradation of dilute tri-n-octylamine solution introduces some uncertainty into the results shown in Table 9. The degradation rates measured here indicate that the amount of degradation during those tests was probably small, and that in continuous process operations it would probably be negligible in comparison with other normal losses.

Table 10

EFFECT OF PROLONGED AGING ON DILUTE AMINE SOLUTIONS

Amine	Cmpd.	Diluent	Molarity* of Amine				Date
			Total	Primary	Secondary	Tertiary	
Didecyl	47G	Benzene	0.128	0.004	0.115	0.009	Nov. 11, 1954
			.126	.002	.114	.009	May 23, 1955
Di(2-butyloctyl)	198A	Kerosene	~0.10	0.001	0.097	0.002	Oct. 7, 1954
			.088	.008	.080	.000	May 23, 1955
"	198A	"	~0.10	0.001	0.097	0.002	Oct. 7, 1954
			.098	.006	.092	.000	May 23, 1955
Methyl-di-(2-ethylhexyl)	134A	Benzene	0.120	0.000	0.001	0.119	Nov., 1954
			.079	.003	.019	.057	May, 1955
Tri-n-octyl**	125H	Kerosene	0.099	<0.001	<0.001	>0.098	Oct., 1954
			.093	.004	.012	.077	Feb., 1955
			.077	.006	.017	.054	May 24, 1955
Mixed n-octyls		Benzene	0.093	0.022	0.033	0.037	Nov. 11, 1954
			.092	.017	.038	.037	May 23, 1955

*Total molarity by direct acidimetric titration. Molarity of primary, secondary, and tertiary components are calculated from differential titrations on the assumption that these three classes of simple amines are the only titratable bases present.

**The analysis of the freshly-prepared tri-n-octylamine solution, October, 1954, corresponded to >99% tertiary, <1% primary + secondary. Samples of the (undiluted) amine taken in June, 1955, again showed >99% tertiary and <1% primary + secondary. These samples were taken both from a freshly-opened can and from a can which had been partially emptied in October, 1954.

Reaction with Diluents. The amine stability tests described so far were all made with benzene, kerosene, or kerosene-alcohol as the diluent, but not with the aromatic mineral spirits which have been used extensively in other studies of the amines. This is because the aromatic mineral spirits Amsco G and D-95 were found to contain significant amounts of materials which react slowly with the amines, in addition to the other types of reactions that might be occurring simultaneously. Table 11 shows the results of some typical aging tests of amines in these two diluents as compared with kerosene. These values are the decreases in molarity as given by simple titrations made before and after storing for 14 days. Figure 3 gives the actual initial, intermediate and final molarities for three of these tests, showing the rate of decrease with time. (The curves indicate that the reaction was levelling off but not complete at 14 days.)

Qualitative tests of the aromatic mineral spirits showed that Amsco G and especially Amsco D-95 contain considerable quantities of unsaturated materials reactive with permanganate and with bromine (producing hydrogen bromide), and also some acidic material. This suggests that the degradation could be eliminated by a suitable pretreatment of the diluent. So far only water-washing and permanganate oxidation have been tested, and these only cursorily. The results, Table 12, show some amelioration of the large loss in Amsco D-95, but essentially no effect on the smaller loss in Amsco G. The much smaller loss in kerosene solution, included for comparison, was also unaffected by this pretreatment.

Since these aromatic diluents are otherwise useful in combination with a wide variety of amine types, it is expected that some further attention will be given to the type of pretreatment required to minimize the reactive impurities.

Conclusions. From consideration of all the foregoing tests, it may be concluded that the secondary amines tested appear to be essentially free from oxidation or other deleterious reaction under conditions likely to be encountered in process use at ambient temperatures. For the tertiary amines the results appear less clear-cut, and they are found to react to a greater extent than the secondary amines under some special conditions. However, they also appear to be sufficiently free from such reactions for satisfactory use under the conditions most like to be encountered.

Table 11

REACTION OF AMINES WITH DILUENTS

Amine[a]	Batch	Net Decrease of Amine Concentration, ΔM, in 14 days					
		Amsco D-95		Amsco G		Kerosene	
		Dark	Light[b]	Dark	Light[b]	Dark	Light[b]
Trioctyl	116F						
(basic form):		0.006	0.006	0.004	0.005	0.003	0.003
(sulfate)[c]:			.004		.004		
Didecyl	47G						
(basic form):		.015	.020	.011	.012	.000	.000
(sulfate)[c]:			.002		.005		
Armeen 2-12	103F						
(basic form):		.014	.017	.008	.008	.001	.002
(sulfate)[c]:			.006		.002		

a) Initial amine concentrations in range 0.05 to 0.1 M.

b) Normal room (fluorescent) lighting.

c) The amine solution was equilibrated at $4^a:1^o$ with 0.5 M sulfate solution, pH 1.1, immediately after it was made up. (The aqueous phase was not present during the rest of the test.)

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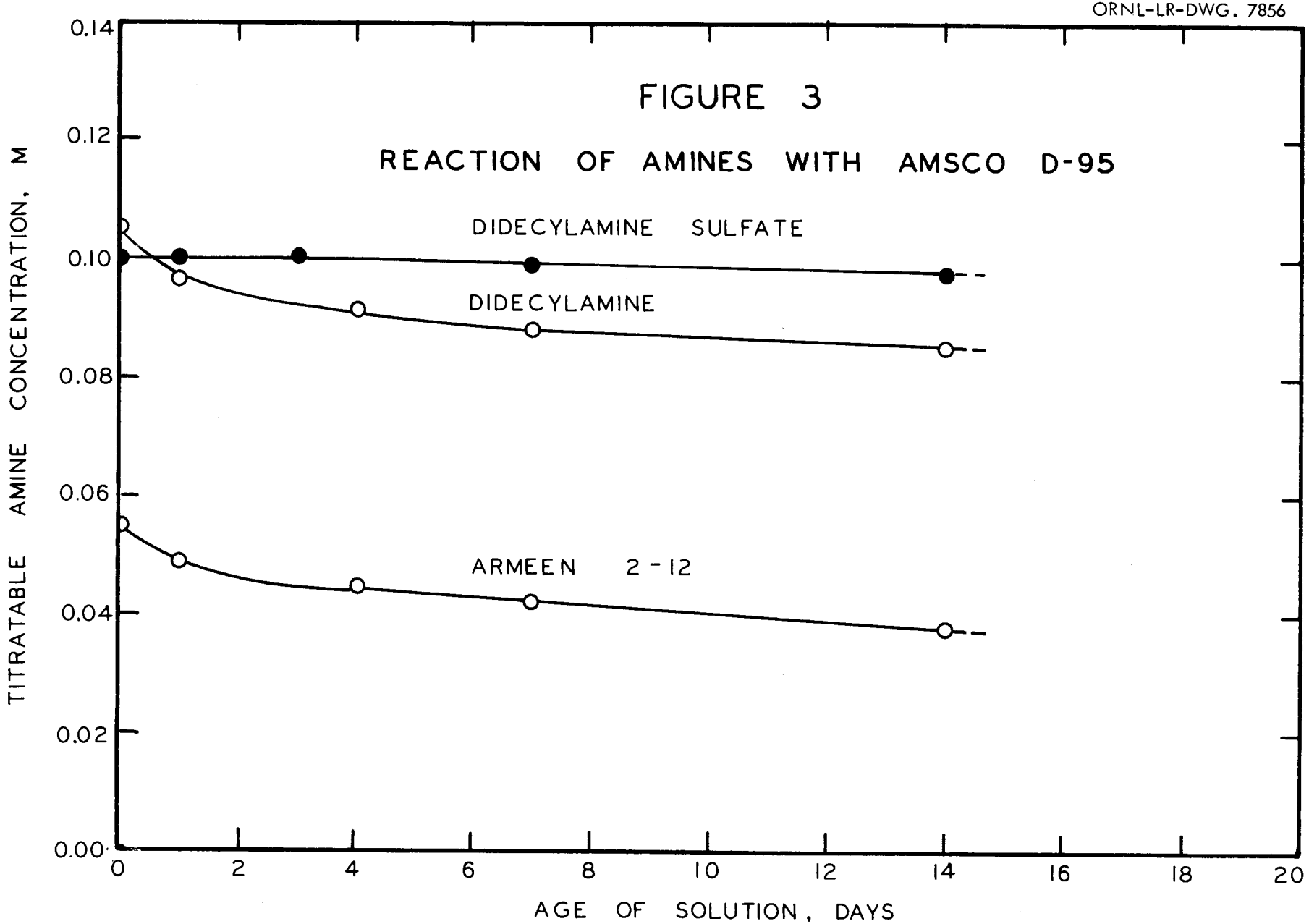

Table 12

REACTION OF ARMEEN 2-12 WITH TREATED DILUENTS

Pretreatment of Diluent	Net Decrease of Amine Concentration, ΔM, in 30 days		
	Amsco D-95	Amsco G	Kerosene
Untreated	0.019	0.005	0.002
Water-Washed	.018	.005	.002
Oxidized	.013	.006	.002

Initial amine concentration in range 0.06 to 0.1 M.

Normal room (fluorescent) lighting.

Water wash: Amine solution washed six times with half-volume portions of water.

Oxidation: Amine solution treated with successive half-volume portions of 1% $KMnO_4$ solution until there was no change of color; then washed with three half-volume portions of water.

F. POTENTIAL AVAILABILITY AND COST OF AMINES

In selecting amines for possible practical application, the potential cost and availability of the compounds must be considered in conjunction with their chemical and physical extraction properties. Although the amines showing greatest promise in the screening tests are presently available in experimental quantities only, it has been possible in most cases to obtain helpful information regarding their potential cost and availability through written or verbal communication with the probable suppliers. A brief summary of the information obtained in regard to several of the more promising compounds studied is itemized below. Almost all of the compounds would be made available in large quantities in the event of a demand. The estimated selling prices for many of the compounds are such as to make them likely candidates for a practicable process application.

The potential cost of the amines would be governed to a reasonable extent by the size of the demand. For most discussions of potential costs with suppliers an arbitrary demand of 100,000 to 300,000 lbs/yr was ordinarily postulated. From the overall tenor of the discussions it was apparent that larger demands, i.e., in the order of one million pounds per year, would cause a general move toward lower prices and cause even a wider variety of compounds to be brought into the area of active consideration. Sales in the order of a million pounds per year are reasonably large in the organic chemical industry and would be sufficient to create considerable competitive development work and sales effort.

Amine 9D-178 (from Rohm and Haas)

The following comments were made by the supplier[6].

"Based on the one pilot plant batch of Amine 9D-178 [dodecenyl Primene 81 amine] we have made, we gave you a very rough price estimate of 60¢ - $1.00 per pound for commercial production. I would like to say again that this is based on limited process study, and I am sure that this estimate could be refined much further after we have studied the process more. I believe that any changes on further study should certainly be in the direction of decreased price."

Another amine of similar structure but higher molecular weight (dodecenyl Primene JM amine) has been

recently submitted to this laboratory by Rohm and Haas. This amine would reportedly sell at a somewhat higher price but has an advantage in a lower loss through distribution to aqueous liquors[7]. Its pertinent extraction characteristics are being evaluated.

Armeen 2-12 (mostly dilaurylamine) (from Armour)

In discussions with representatives of the Armour Chemical Division an estimate of 60-70¢ per pound was given (verbally) as the potential selling price of Armeen 2-12, satisfactory in purity for the intended application[8].

Tri-n-octylamine (from Carbide)

The following comments were made by the supplier[9].

"Regarding tri-n-octylamine, ... we would never classify this material as anything under $1.50 per pound chemical, even if a large volume use were to develop. For your discussions, we feel that the $1.50 per pound price would be realistic for you to use."

More recently, however, the opinions with regard to tri-n-octylamine have been revised. In discussions with Carbide research and development people, it was mentioned that this compound might lend itself to preparation by more simplified procedures on a production basis than had been considered previously and that further development work might indicate production at lower costs than mentioned above[10].

Di(2-butyloctyl)amine (from Carbide)

On the basis of laboratory work only, the cost would probably be $1.00 per pound or possibly greater (as per discussion with supplier[10]).

C&CCC 16F27 (from Carbide)

Would probably be less than $1.00 per pound[10].

N-(2-ethylhexyl)-1-isobutyl-3,5-dimethylhexylamine (from Carbide)

Would probably be less than $1.00 per pound[10].

Di(Tridecyl P)amine (from Carbide)

Could be in the 60¢ - $1.00 per pound range[10].

Bis(1-methyl-4-ethyloctyl)amine (from Carbide)

About the same range as di(2-butyloctyl)amine[10].

Di(OxoDecyl)amine (from Carbide)

Could be in the 60¢ - $1.00 per pound range[10].

N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine (from Carbide)

Because of the current high price and limited supply of heptadecanol (i.e., 1(3-ethylpentyl)-4-ethyloctanol) the amine would be fairly expensive, i.e., greater than $1.00 per pound and probably significantly greater[10].

This compound (and similar compounds) is worthy of further attention, however, because of its unusually high extraction power. The high extraction coefficients (and low loss to aqueous solutions) would be particularly attractive when dealing with low grade uranium liquors. The possibilities of such reagents have been described to workers at Columbia University who are interested in the recovery of uranium from uraniferous shales[11].

Trilaurylamine (from Armour)

The following comments were made by the supplier[12].

"..... We (Armour) are in no position to commit ourselves. I would say, though, that a price of $1.00/lb is probably a minimum estimate."

Tri-n-decylamine would be comparatively less attractive than trilaurylamine from Armour's standpoint because of the lower availability of the decyl radicals (from coconut oil)[8].

Information regarding availability and cost has not been obtained for many other amines which have shown promise in the screening tests, e.g., lauryldihexylamine, dihexyl(Tridecyl P)amine, di(Nonyl B)butylamine, and other similar unsymmetrical tertiary amines; methyldidecylamine, and other methyldialkylamines; benzyllaurylamine, benzyldilaurylamine, and other amines with aromatic substituents; etc. The organic radicals contained by these amines are, however, available or potentially available, and consequently the amines may also be considered as potentially available. This would also be true for amines different in type but containing the same organic radicals as contained by the compounds listed previously. The general range of prices for these compounds should be similar to those for the compounds already described. Again, the price ranges would be expected to vary with the extent of demand.

Those amines which "passed" the screening tests and which appear to be nearest to commercial production at the lowest estimated costs were chosen for the initial large scale development tests at this laboratory. Thus, runs, to be reported separately, have been made in the large scale process test facility with R&H 9D-178 amine and Armeen 2-12. According to present plans the next runs will be made with di(Tridecyl P)amine. The amines tested have given good process performance. The information obtained has, however, not been sufficient to establish whether or not the amines of lower cost are necessarily the most advantageous for process use. Reagent (amine) losses in the process cycle have been small and it is possible that the initial costs for more expensive reagents could be offset, provided the reagents possessed operational advantages in the way of physical performance, selectivity, etc. Further large scale tests will be made to obtain a clearer understanding of the balance between reagent cost and operational efficiency.

Several secondary amine mixtures are commercially available at this time. Although the use of some of these (see below) might be possible, their general extraction performance characteristics have been markedly inferior to other promising experimental reagents described above, which could also be made commercially available at a reasonable cost in the event of a demand.

Armeen 2C (Armour and Company, ~50¢/lb)

A commercially available mixture of fatty secondary amines (ordinarily about 85% secondary amine content) with the following approximate composition: 8% octyl, 9% decyl, 47% dodecyl, 18% tetradecyl, 8% hexadecyl, and 10% octadecyl. The alkyls are derived from coconut oil.

This secondary amine mixture has shown diluent compatibilities and phase disengagement properties which are poorer than Armeen 2-12 and much poorer than the promising branched chain secondary amines. Like the straight chain secondary amines in general, it also has limited compatibility with chloride or nitrate stripping procedures. It is, however, commercially available and might be of potential use. It has been retained in the evaluation program.

Another secondary fatty amine of higher average molecular weight, Armeen 2HT, commercially available from Armour has not given effective performance.

Armeen 2S and 2T (Armour and Company, ~40¢/lb)

Commercially available mixtures of partially unsaturated fatty secondary amines (ordinarily about 85% secondary amine content) with the following approximate compositions: for 2S - 10% hexadecyl, 10% octadecyl, 35% octadecenyl and 45% octadecadienyl; for 2T - 30% hexadecyl, 25% octadecyl and 45% octadecenyl. The alkyls are from soybean oil and tallow, respectively.

These materials, in some instances, have shown somewhat better (but still limited) compatibility with ordinary kerosene than the saturated secondary amines. They do not, however, compare favorably to the branched secondary amines in this respect. Also considerable variations have been noted between batches. One batch of Armeen 2T was not useable because of limited solubility in the diluent. In regard to phase separations, these materials compare unfavorable to the other promising reagents tested and they compare unfavorably to the branched secondary amines in regard to compatibility with chloride and nitrate stripping. A mixed low-purity reagent of this type would add complexity to a solvent extraction process. It is, however, commercially available and although its performance characteristics are comparatively poor, it has been retained in the evaluation program pending further investigation.

As described previously some of the primary amines tested have shown good extraction of uranium from pure sulfate solutions but have poor selectivity for uranium with respect to ferric iron. They do not, however, extract ferrous iron and might be applicable if the iron in the liquor was reduced. The primary amines are also effective extractants for most tetravalent metals from sulfate solutions and the use of these compounds in thorium processing has been proposed[3].

The only commercially available primary amine which is of interest from tests thus far is Primene JM-T (Rohm and Haas, ~50¢/lb). This product is a mixture of long branched-chain, 18-24 carbon, primary amines with the nitrogen bonded to a tertiary carbon.

Other primary amines of lower molecular weight available from Rohm and Haas, Primene 81T and tertiary - octylamine, are not of interest as extractants due to high reagent losses to the aqueous liquors. Primary amines commercially available from other sources, i.e., Armeens 12, 16, 18, C, S, T, HT and Rosin Amine D, have not shown good extraction performance.

IV. SUMMARY

Since the first report on the use of amines as uranium extractants (ORNL-1734) over eighty additional organo-nitrogen compounds have been examined for their ability to extract uranium from aqueous solutions, particularly sulfate solutions, of the types usually encountered in uranium ore processing. As before, the more promising of these (as well as other compounds previously reported) have been examined further with respect to other characteristics essential to practical application, i.e., low reagent loss to the aqueous phase, compatibility with practicable diluents, reagent stability, sufficient selectivity for uranium, adequate phase separation properties, compatibility with practicable stripping methods, etc. The potential cost and availability of the reagents have also been considered. The principle conclusions to be drawn from these recent tests may be listed as follows:

1. Several of the amines recently tested were effective extractants for uranium from acidic sulfate liquors. Taking into account the other criteria for a practical reagent as listed above, as well as uranium extraction ability, the more promising of these newer reagents are:

N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine
Di(2-butyloctyl)amine
R&H 9D-178 Amine (dodecenyl Primene 81)
Di(Tridecyl P)amine
Benzyldilaurylamine
Bis(1-methyl-4-ethyloctyl)amine

Di(OxoDecyl)amine
Dihexyl(Tridecyl P)amine
Benzyllaurylamine

Possibly Armeen 2S and 2T

Most of the promising compounds tested are presently available in experimental quantities only. However, several of these listed above, as well as some showing promise in previous studies, could apparently be made available at reasonable prices (60¢ - $1.00/lb) in the event of a demand, e.g., R&H 9D-178, Armeen 2-12, C&CCC 16F27, di(Tridecyl P), and di(OxoDecyl)amines. Several other compounds can apparently also be considered as potentially available at a higher price ($1.00 - $1.50/lb, depending to some extent upon the size of the demand),

e.g., di(2-butyloctyl), tri-n-octyl, and possibly tri-lauryl amines. The higher initial costs of these latter reagents would not necessarily be prohibitive.

2. The compounds listed in the first group under (1) above (most of which are highly branched secondary amines) showed good compatibility with ordinary kerosene as the diluent. Several of the reagents tested thus far, i.e., R&H 9D-178, N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine, di(2-butyloctyl)amine, and di(Tridecyl P)amine, were retained by the kerosene at concentrations greater than 0.6 M even when contacted by sulfate solutions of low pH, where most of the reagent would be converted to the ordinarily less miscible bisulfate form. With such a miscibility range, kerosene should be a suitable diluent for these reagents even in applications wherein the uranium concentration levels may demand a rich extracting phase. The other reagents listed were not compatible with kerosene alone but gave good performance if the kerosene was modified with a small amount (2-5% v/v) of a long-chain alcohol. Amsco D-95 and Amsco G continued to show good compatibilities with the widest variety of amines, all of those listed giving good performance in these diluents. These diluents may have a disadvantage in addition to their higher initial cost, however, since it has been observed that minor constituents present can react with the amines and render the reacted portion inert to the extraction process. This effect could be a point of concern in establishing purchasing specifications for these solvents.

3. One of the new reagents listed above, N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine, gave much higher uranium extraction coefficients than have been obtained with any other organonitrogen compound tested. Accordingly, a fuller investigation is being made of this compound, and also of others of similar structure.

4. Loss of reagent through distribution to the aqueous phase was very low (<5 ppm) for several of the newer amines tested, e.g., di(2-butyloctyl)amine, di(Tridecyl P)amine, N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine, bis(1-methyl-4-ethyloctyl)amine, dihexyl(Tridecyl B)amine, and Armeen 2T. Losses of R&H 9D-178, C&CCC 16F27, and di(OxoDecyl)amine were significant but not sufficient to prevent their use in process application. Several compounds, such as Primene JMR, R&H 9D-178, di(Tridecyl P), bis(1-methyl-4-ethyloctyl), C&CCC 16F27, dihexyl(Tridecyl B), and di(OxoDecyl)amines, showed a significant initial solubility loss. In the first four cases this loss was reasonably small and, in process application, would be

reflected as a moderate increase in the purchase price of the amine. With the latter three, however, the initial loss was high. If these materials are representative of those expected from commercial production, a very low comparative selling price would be required for them to be competitive with the other promising reagents.

5. As also noted in earlier work, several factors were observed to influence the losses of amines to the aqueous phase. For example: Under a given set of conditions the loss into sulfate solution is less at higher pH; the loss into a given solution can be dependent on the diluent, a greater loss usually being incurred from kerosene than from benzene; and, for a specific type of amine, the losses of the individual amines to a given solution are primarily related to their molecular weights. In addition to these relationships, some recent tests have shown that the distribution of amine to the aqueous phase is decreased by the presence of a long-chain alcohol and also by the presence of uranium.

6. Preliminary studies of stability indicated that the secondary and tertiary amines tested are sufficiently free from oxidation or other deleterious reactions for satisfactory use under the conditions most likely to be encountered in process applications. Measurable degradation occurred under some special conditions, as in the presence of oxidizing agents at elevated temperatures ($50^{o}C$), or under strong illumination, the tertiary amines reacting more readily than the secondary amines.

7. Separations of uranium from thorium in sulfate solutions were achieved very effectively by extracting with a symmetrical tertiary amine. Good separations were also obtained by extracting with a secondary amine.

8. Extractions of titanium from sulfate solutions were low with the straight-chain secondary amines and lower with the highly branched secondary and symmetrical tertiary amines. In contrast, appreciable extractions were obtained with the primary amines. These variations in extraction with amine types are qualitatively similar to those obtained with other tetravalent metals. Variation in extraction as a function of liquor composition also appeared similar to those noted with other metals, i.e., the extraction appeared to decrease with increasing sulfate concentration and increase with increasing pH.

9. The general selectivity properties as noted for the recent amines tested were in general accordance with trends established in previous studies. Thus, the

symmetrical tertiary amines have shown the best selectivities with respect to iron and most tetravalent and other metals; the selectivities of the highly branched secondary amines are superior to those with no branching or branching at a distance from the nitrogen; the primary amines have comparatively poor selectivity properties. Molybdenum is extracted, of course, by all of the amines tested.

10. A few "miscellaneous organonitrogen compounds" (compounds other than the simple amines) showed ability to extract uranium from sulfate solutions but were unacceptable with respect to phase separation and solvent compatibility, e.g., N-decylpiperidine, N-"tallow"-morpholine, and N-"coco"-morpholine. Many other compounds in this category that were tested were ineffective as extractants. However, as before, most of these reagents were those which happened to be at hand or easily obtainable and were not necessarily of optimum molecular weight, etc., for use in solvent extraction. Consequently, the results merely suggest again that some organonitrogen compounds, other than the simple amines, may prove satisfactory for uranium extraction, and no generalization can be made until a wider variety of compounds have been examined.

11. Moderate extraction power for uranium from carbonate solutions was shown by several quaternary ammonium salts in chloroform, i.e., cetyldimethylbenzylammonium sulfate and chloride, the sulfate and chloride salts of Hyamine 10X, and the sulfate and chloride salts of Hyamine 1622. Benzene was not a suitable diluent for these compounds. On the basis of the moderate encouragement given by these results, further studies will be made to cover a wider variety of compounds, diluents and extraction conditions.

It is generally apparent from the recent studies with organonitrogen compounds that, as in previous work, most of the compounds originally considered were found worthy of only cursory examination. On the other hand, the important outcome again has been that several compounds, particularly several long branched-chain secondary amines, have been found to have considerable promise for practicable solvent extraction application. In some cases the properties of these new reagents are more favorable than those of most compounds previously tested.

Some of the better reagents have been subjected to laboratory-scale process studies with excellent results.

Two of these, i.e., Armeen 2-12 and R&H 9D-178, have been examined by the Engineering Group in the larger-scale process test facility with successful performance being given. The results from the laboratory and larger-scale process tests are being reported separately. Laboratory screening type tests are continuing in study of newer reagents and new applications.

V. ACKNOWLEDGEMENTS

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Many of the reagents which were obtained from outside sources were furnished as product samples by the manufacturers. In addition, special reagents were contributed by the research laboratories of Carbide and Carbon Chemicals Company and of Rohm and Haas Company.

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APPENDIX A

EFFECTS FROM FLUORIDE ON THE EXTRACTION OF URANIUM FROM SULFATE SOLUTIONS

Results from extraction studies made by contacting dilauryl- and tri-n-octylamine solutions with acidic sulfate solutions containing uranium and various quantities of fluoride were reported previously (cf. ORNL-1734, Table 9). Similar studies have since been made with didecyl- and methyldidecylamine. These results may be found in Table 13 with a graphic comparison of these and the previous results in Figure 4. In all cases the extractions were found to decrease with increasing fluoride concentration.

As before, however, it must be pointed out that these tests were made with "pure" uranium solutions and that different effects were noted in extractions from contaminated solutions such as ore leach liquors. In these solutions the fluoride can complex strongly with other metals such as iron and molybdenum and thus reduce their extraction. The overall effect from the presence of fluoride can, therefore, be sometimes of benefit both to the extraction coefficient and to the selectivity of uranium separation.

Extraction Of Uranium From Fluoride Solutions

Extraction of uranium from aqueous fluoride solutions is shown in Table 14. In these tests, the initial uranium concentration was about 1 g/l; the amine used was tri-n-octyl, 0.1 M in D-95, pretreated with a dilute hydrofluoric acid solution to be in equilibrium at a pH of 2. Fluoride concentrations below 2 M were favorable for uranium extraction, while at higher concentrations the extraction decreased rapidly. This is in contrast to the increase of uranium extraction from chloride solutions with increasing chloride concentration (ORNL-1734, Table 15). These extraction patterns are similar to the uranium sorption patterns found with anion exchange resins in fluoride and chloride systems (Y-816, p. 52). They probably reflect the different effectiveness of these two halides in forming uranium complexes suitable for extraction. The uranium is extensively complexed by even low

Table 13

EFFECT OF FLUORIDE CONCENTRATION ON EXTRACTION OF URANIUM(VI) FROM ACIDIC SULFATE SOLUTION BY AMINES

Amine	F^- Mol.	U E_a^o
Didecyl	0.00	39
	0.16	5
	0.32	2.6
	0.52	2
	0.79	1
Methyldidecyl	0.00	19
	0.16	1.1
	0.32	0.5
	0.52	0.3
	0.79	0.0095
	1.00	0.0017

Extraction Conditions:

Organic = 0.1 M amine in D-95
Aqueous = 1 g/l U, 1 M SO_4, pH = 1
Phase Ratio = 2 aqueous:1 organic

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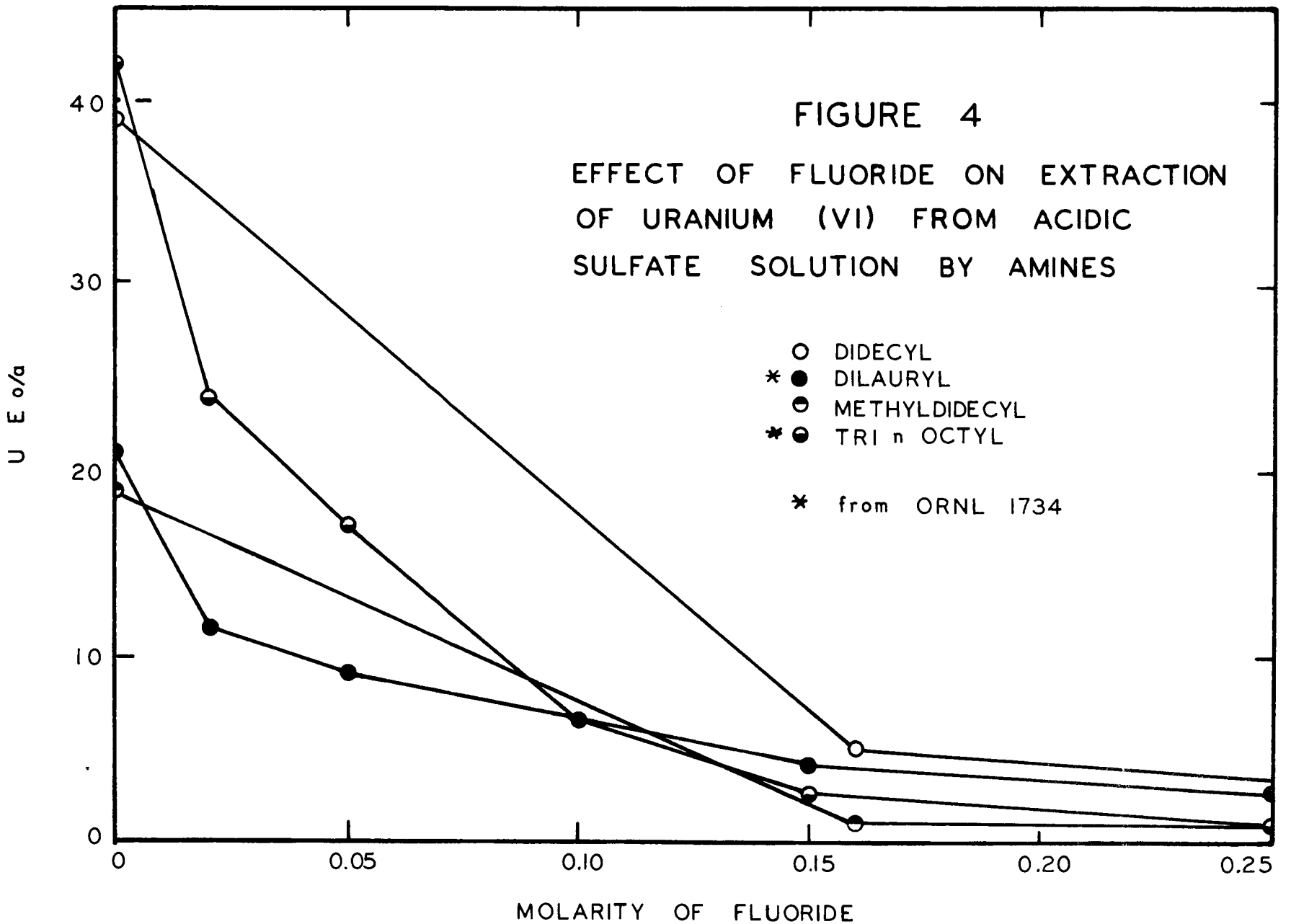


Table 14

EXTRACTION OF URANIUM FROM FLUORIDE SOLUTIONS

F^- Mol.	Initial pH	Final pH	U E_a^o
0.5	1.30	1.40	140
1.0	1.00	1.15	35
2.0	1.05	1.10	5
3.0	1.00	1.10	1.6
4.0	1.05	1.15	.3
5.0	1.00	1.10	.1

Extraction Conditions:

0.1 M Trioctylamine (Cmpd. 116) in Amsco D-95 pretreated with HF solution to be in equilibrium at pH = 2.

Aqueous = 1 g/l U.

Phase Ratio = 2 aqueous:1 organic.

fluoride concentrations, and additional fluoride competes for the amine and/or forms less favorable complexes, but it is not sufficiently complexed by chloride unless the concentration is fairly high.

The effects of chloride and fluoride on uranium extraction from sulfate solution were rather similar (above), but these results indicate that the reasons for the interference were different. Chloride probably competed for the amine, leaving more of the uranium sulfate complex in the aqueous solution, while the fluoride probably competed for the uranium (as a less favorably extracted aqueous complex), while more of the amine remained as the free sulfate salt.

APPENDIX B

NONAQUEOUS TITRATION OF AMINES

Recent publications[4] report that amine concentrations in organic solvents may be determined efficiently and precisely by nonaqueous titration methods. The procedure used at this laboratory, and described below, was drawn from these publications.

Reagents:

0.05 N perchloric acid. Dilute 8.5 mls of 72% perchloric acid to 2 liters with 1,4-dioxane, Eastman White Label, that has been contacted with the hydrogen form of Dowex-50.

Diphenylguanidine. The technical grade material is purified by recrystallization first from toluene, next from 95% ethyl alcohol, and then from toluene again.

Procedure:

A sample of 2-5 mls of the organic phase containing amine is added to approximately 75 mls of chloroform and the solution titrated with 0.05 N perchloric acid, previously standardized against diphenylguanidine. The titrations are followed with either a Beckman G pH meter or a Precision Dow Recordometer Titrator using ordinary glass and calomel electrodes. To obtain steady potential readings the circuit resistance is decreased by placing the tips of the electrodes as close together as possible.

Most of the titrations at this laboratory have been made on solutions containing free amine. Solvents containing amine salts have ordinarily been treated with an aqueous carbonate or hydroxide solution to convert the salts to the free amine form. It is possible, however, to titrate the amine sulfates directly, according to the following reaction:

$$(RNH_3)_2^+ SO_4^= + H^+ClO_4^- \rightarrow 2RNH_3^+ + HSO_4^- + ClO_4^-$$

This titration permits a measurement of both the amine sulfate and bisulfate in the reagent solution. Thus, the

sulfate is first determined by titrating the amine salt. Next an aliquot is converted to free amine by contacting the reagent with an aqueous solution of sodium hydroxide, and the total amine content determined. This value minus twice the value obtained in the sulfate titration gives the amount of amine in the bisulfate form.

Nonaqueous titration methods also offer a means for quantitatively differentiating the primary, secondary and tertiary contents of an amine mixture containing no other titratable base. In this case, the total amine content is first obtained by titrating a sample of the mixture according to the method outlined above. The secondary plus tertiary fraction is next determined by reacting an aliquot of the mixture with salicylaldehyde and retitrating. Any primary amine present reacts with the aldehyde to form a Schiff base which is very weak and may be distinguished from the secondary and tertiary amines.

$$R - \overset{H}{C} = O + H_2N\text{-}R \longrightarrow R - \overset{H}{C} = N - R$$

The tertiary amine content is determined by reacting another aliquot of the original mixture with acetic anhydride plus acetic acid and again titrating. The primary and secondary amines will react with the acetic anhydride (see below) whereas the tertiary amine lacks a replaceable hydrogen and cannot be acylated. In some cases in which the secondary amine is severely sterically hindered the reaction will not take place, but fortunately this much steric effect is not often found.

$$CH_3\text{-}\overset{O}{C}\text{-}O\text{-}\overset{O}{C}\text{-}CH_3 + H\text{-}\overset{H}{N}\text{-}R \longrightarrow CH_3\text{-}\overset{O}{C}\text{-}\overset{H}{N}\text{-}R + CH_3\text{-}\overset{O}{C}\text{-}OH$$

$$CH_3\text{-}\overset{O}{C}\text{-}O\text{-}\overset{O}{C}\text{-}CH_3 + H\text{-}\overset{R}{N}\text{-}R \longrightarrow CH_3\text{-}\overset{O}{C}\text{-}\overset{R}{N}\text{-}R + CH_3\text{-}\overset{O}{C}\text{-}OH$$

$$CH_3\text{-}\overset{O}{C}\text{-}O\text{-}\overset{O}{C}\text{-}CH_3 + R\text{-}\overset{R}{N}\text{-}R \longrightarrow \text{No reaction}$$

The details of the procedure used at this laboratory for differentiating the primary, secondary and tertiary content of a mixture are as follows:

A. Total Amine

A 0.5 to 0.1 M solution of the reagent in question is prepared in benzene. A 5 ml aliquot is added to ~75 mls chloroform and titrated with 0.05 N $HClO_4$ in 1,4-dioxane.

B. Secondary plus Tertiary Amine

A 5 ml aliquot of the benzene solution is mixed with 2 mls of salicylaldehyde (from bisulfite addition compound) and allowed to stand for at least 30 minutes at room temperature. Approximately 75 mls of chloroform is then added and the solution titrated to the first end-point. In mixtures containing only small amounts of primary amine, it is often difficult to distinguish the first end-point from the second. With these, one ml of a 0.1 M solution of pure primary amine is added to the reagent aliquot at the same time as the salicylaldehyde.

C. Tertiary Amine

Ten mls of the benzene solution is mixed with 10 mls of acetic anhydride and 1 ml of acetic acid. The mixture is refluxed gently for 1 hour, allowed to cool and titrated as before.

From these three titrations a mixture of primary, secondary and tertiary amines can be completely analyzed.

$$\% \text{ Primary} = \frac{A - B}{A} \times 100$$

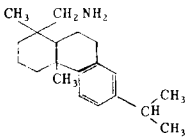
$$\% \text{ Secondary} = \frac{B - C}{A} \times 100$$

$$\% \text{ Tertiary} = \frac{C}{A} \times 100$$

APPENDIX C

DESCRIPTION OF COMPOUNDS

Primary Amines

Amine	Source[c]	Formula	Description[b]	Mol. Wt.[a] Theo.	App
Furfuryl	CS	CH:CHCH:C-CH_2-NH_2 (O)	~99% Furfuryl amine[b]	97	99
Octyl (tertiary)	RH	$(CH_3)_3$-C-CH_2-C($CH_3)_2$-NH_2	Laboratory sample, < 1% H_2O[b]	129	129
Dehydroabietyl (Rosin Amine D)	H		91% Amine[b]	285	307

Secondary Amines

Di(OxoDecyl)	C	$(C_{10}H_{21})_2$ NH	Mixture of C_{10} secondary amines[b]	298	317
Di(2-butyloctyl)	C	$(C_6H_{13}$-CH(C_4H_9)$CH_2)_2$NH	1% Primary, 97% secondary, 2% tertiary	354	355
Bis(1-methyl-4-ethyloctyl)	C	$(C_4H_9$-CH(C_2H_5)-$(CH_2)_2$-CH(CH_3)-$)_2$NH	< 1% Primary, 98+% secondary, 1+% tertiary	326	325
N-(2-ethylhexyl)-1-isobutyl-3,5-dimethylhexyl	C	$(CH_3)_2CHCH_2$-CH(CH_3)-CH_2-CH($CH_2CH(CH_3)_2$)-NH-CH_2-CH(C_2H_5)-C_4H_9	Laboratory sample.	298	298
Di(Tridecyl B) (Cmpd. 162A)	OR	$(C_{13}H_{27})_2$NH with the alkyl group derived from tri-isobutylene	Analysis - C 81.98, H 14.29, N 3.59% Theo. - C 81.81, H 14.52, N 3.67%	382	392
Di(Tridecyl B) (Cmpd. 218A)	C	$(C_{13}H_{27})_2$NH with the alkyl group derived from tri-isobutylene	1% Primary, 99% secondary	382	410
Di(Tridecyl P) (Cmpd. 227A)	C	$(C_{13}H_{27})_2$NH with the alkyl group derived from tetrapropylene	9% Primary 91% secondary	382	371
R&H 9D-178 (Cmpd. 193B)	RH	$C_{12}H_{23}$-NH-C(R')(R'') where R is a highly branched 9-12 carbon alkyl group	-----		378
(Cmpd. 193C)	RH		6% Primary, 94% secondary + tertiary		371
(Cmpd. 193D)	RH		-----		371
Bis(1-isobutyl-3,5-dimethylhexyl)(16F27)	C	$((CH_3)_2CHCH_2$-CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH(CH_3)-$CH_2)_2$NH	Laboratory sample	354	348
Armeen 2S	AR	R_2NH, where R is unsaturated with a mol. wt. from 520-540[b]	1% Primary, 76% secondary, 23% tertiary		567
Armeen 2T	AR	R_2NH, where R is unsaturated with a mol. wt. from 520-540[b]	85% secondary, 15% tertiary		550
7-Aminomethyl-1,4-dimethyl-6,8-dioxa-bicyclo (3.2.1) octane	C	H_2NCH_2-CH-O / CH_3-C - O-CH / CH_2CH_2-CH-CH_3	Laboratory sample	170	171
Benzyllauryl	OR	$C_6H_5CH_2NH(CH_2)_{11}CH_3$	Analysis - C 83.0 , H 11.6 , N 5.3 % Theo. - C 82.84, H 12.08, N 5.09%	275	275
N-Benzyl-1(3-ethylpentyl)-4-ethyloctyl	C	C_4H_9-CH(C_2H_5)-CH_2-CH(NH-CH_2-C_6H_5)-CH_2-CH-CH_2-CH(C_2H_5)$_2$	2% Primary, 95% secondary, 3% tertiary	347	348
Phenyl-β-naphthyl	G	$C_{10}H_7$-NH-C_6H_5	Laboratory sample	219	
p-Isopropoxydiphenyl	G	C_6H_5-NH-C_6H_4OCH($CH_3)_2$	Laboratory sample	227	
Phenylethanol	C	$C_6H_5NH(C_2H_4OH)$	Laboratory sample	137	
α-Methylbenzylethanol	C	C_6H_5-CH(CH_3)NH(C_2H_4OH)	Laboratory sample	165	
o-Tolylethanol	C	$C_6H_4(CH_3)$-NH-(C_2H_4OH)	Laboratory sample	151	

DESCRIPTION OF COMPOUNDS

Tertiary Amines

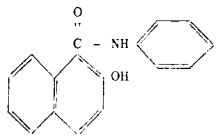
Amine	Source[c]	Formula	Description[b]	Mol. Wt.[a] Theo.	App.
N,N-dimethyl-Soy	AR	R-N-$(CH_3)_2$ where R is from soy oil	Laboratory sample		333
Tri-n-octyl (Cmpd. 125H)	C	$(CH_3(CH_2)_7)_3N$	>99% Tertiary amine	354	350
Di(Nonyl B)butyl	C	$C_4H_9N(C_9H_{19})_2$	1% Primary, 16% secondary, 83% tertiary	326	320
Dihexyl(Tridecyl B)	OR	$(C_6H_{13})_2N(C_{13}H_{27})$	Analysis - C 82.05, H 14.3, N 3.81% Theo. - C 81.66, H 14.5, N 3.81%	368	373
Tri(Tridecyl B)	OR	$(C_{13}H_{27})_3N$, where the alkyl group is derived from tri-isobutylene	Analysis - C 82.95, H 14.25, N 2.74% Theo. - C 83.04, H 14.48, N 2.48%	564	565
N-Benzyl-bis(2-ethylhexyl)	C	$C_6H_5CH_2N(-CH_2-\underset{C_2H_5}{CH}-C_4H_9)_2$	Laboratory sample	332	334
Benzyldilauryl	OR	$C_6H_5CH_2N(C_{12}H_{25})_2$	Analysis - C 83.7, H 12.7 , N 3.34% Theo. - C 83.9, H 12.95, N 3.15%	444	444
Dibenzyllauryl	OR	$(C_6H_5CH_2)_2NC_{12}H_{25}$	Analysis - C 84.7, H 10.8, N 4.1% Theo. - C 85.4, H 10.8, N 3.8%	366	385
Phenylmethylethanol	C	$C_6H_5\underset{CH_3}{N}-C_2H_4OH$	Laboratory sample	151	
Phenyldiethanol	C	$C_6H_5N(C_2H_4OH)_2$	Laboratory sample	181	
Phenylethylethanol	C	$C_6H_5\underset{C_2H_5}{N}-C_2H_4OH$	Laboratory sample	165	
α-Methylbenzyldiethanol	C	$C_6H_5\underset{CH_3}{C}HN(C_2H_4OH)_2$	Laboratory sample	209	
m-Tolyldiethanol	C	$C_6H_4(CH_3)-N-(C_2H_4OH)_2$	Laboratory sample	195	
Di(2-ethylhexyl)ethanol	C	$(C_4H_9-\underset{C_2H_5}{C}HCH_2-)_2-N-C_2H_4OH$	Laboratory sample	286	

Quaternary Ammonium Compounds

Quaternary S	A	$[CH_3(CH_2)_n\overline{C(\underset{R}{N})-CH_2CH_2-NR}]Cl$	Laboratory sample	455	
Quaternary O	A	$[CH_3(CH_2)_n\overline{C(\underset{R}{N})-CH_2CH_2-NR}]Cl$	Laboratory sample	450	
Quaternary C	A	$[CH_3(CH_2)_n\overline{C(\underset{R}{N})-CH_2CH_2-NR}]Cl$	Laboratory sample	370	
Hyamine 10X	RH	$\left[(C_6H_5)CH_2\underset{(CH_3)_2}{N}(CH_2CH_2O)_2\underset{CH_3}{C_6H_3}-\underset{(CH_3)_2}{C}-CH_2C(CH_3)_3\right]Cl\cdot H_2O$	Pure monohydrate salt[b]	480	
Hyamine 1622	RH	$\left[(C_6H_5)CH_2\underset{(CH_3)_2}{N}(CH_2CH_2O)_2C_6H_4-\underset{(CH_3)_2}{C}-CH_2C(CH_3)_3\right]Cl\cdot H_2O$	Pure monohydrate salt[b]	466	
Trimethylphenylammonium chloride	EK	$[C_6H_5N(CH_3)_3]Cl$		172	
Cetyldimethylethyl-ammonium bromide (Ammonyx DME)	O	$\left[C_{16}H_{33})\underset{C_2H_5}{N}(CH_3)_2\right]Br$	75% Solution[b]	378	
Cetyltrimethylammonium bromide	ADM	$[(CH_3)_3N(CH_2)_{15}CH_3]Br$	Laboratory sample	364	
Cetyldimethylbenzyl-ammonium chloride	ADM	$\left[CH_3(CH_2)_{15}\underset{(CH_3)_2}{N}-CH_2C_6H_5\right]Cl$	Laboratory sample	396	
Cetylpyridinium chloride	ADM	$[\overline{CH:CHCH:CHCH:N}-(CH_2)_{15}CH_3]Cl$	Laboratory sample	339	
Laurylpyridinium chloride	ADM	$[\overline{CH:CHCH:CHCH:N}-(CH_2)_{11}CH_3]Cl$	85-90%[b]	283	
Tributyllaurylammonium bromide	OR	$[(C_4H_9)_3NC_{12}H_{25}]Br$	Laboratory sample	435	

DESCRIPTION OF COMPOUNDS

Miscellaneous Nitrogen Compounds*

Compound	Source[c]	Formula	Description[b]	Mol. Wt.[a] Theo.	App.
Anilide of BON*	P		Laboratory sample	263	
m-Nitranilide of BON	P		Laboratory sample	323	
p-Nitranilide of BON	P		Laboratory sample	323	
m-Chloranilide of BON	P		Laboratory sample	332	
p-Chloranilide of BON	P		Laboratory sample	332	
o-Toluidide of BON	P		Laboratory sample	277	
p-Toluidide of BON	P		Laboratory sample	277	
4-Chloro-o-toluidide of BON	P		Laboratory sample	312	
5-Chloro-o-toluidide of BON	P		Laboratory sample	312	
m-Xylidide of BON	P		Laboratory sample	291	
p-Anisidide of BON	P		Laboratory sample	293	
o-Anisidide of BON	P		Laboratory sample	293	
Chloranisidide of BON	P		Laboratory sample	328	
Dianisidide of BON	P		Laboratory sample	410	
2,4-Dimethoxy-4-chloro-anilide of BON	P		Laboratory sample	358	
2,5-Dimethoxy-4-chloro-anilide of BON	P		Laboratory sample	358	
2,5-Dimethoxyanilide of BON	P		Laboratory sample	323	
o-Phenetidide of BON	P		Laboratory sample	307	
p-Phenetidide of BON	P		Laboratory sample	307	
α-Naphthylamide of BON	P		Laboratory sample	313	
β-Naphthylamide of BON	P		Laboratory sample	313	
α-Picoline	C	$CH{:}CHCH{:}CHC{:}N$ CH_3	Laboratory sample	93	
2-Methyl-5-ethylpyridine	C	$CH{:}CCH{:}CHC{:}N$ $C_2H_5 \quad CH_3$	Laboratory sample	121	
2-Vinyl-5-ethylpyridine	C	$CH{:}CCH{:}CHC{:}N$ $C_2H_5 \quad C_2H_3$	Laboratory sample	133	
Alkyl Pyridines H.B.	C	Mixture of alkylpyridines	-----		~182
N-Ethylpiperidine	M	$CH_2CH_2CH_2CH_2CH_2-N-C_2H_5$	Laboratory sample	113	
N-Decylpiperidine	OR	$CH_2CH_2CH_2CH_2CH_2-N-C_{10}H_{21}$		225	243
2,5-trans-Dimethyl-piperazine	C	$CH_2C{:}N-CH_2C{:}N$ $CH_3 \quad CH_3$	Laboratory sample	114	
o-Xylidine (3,4-xylidine)	M	$(CH_3)_2-C_6H_3-NH_2$	Laboratory sample	121	
Acetoacetyl-o-tolidine	P	$CH_3COCH_2CONH-C_6H_3-C_6H_3-NH_2$ $CH_3 \quad CH_3$	Laboratory sample	296	
p-Anisidide of 3-hydroxy-benzocarbazole-2-carboxylic acid	P	$C_4H_4-C_6H_2 \diagdown NH$ $HO \diagup C_6H_2$ $CONH-C_6H_4-OCH_3$	Laboratory sample	382	
p-Methoxy-o-methylanilide of 3-hydroxybenzocar-bazole-2-carboxylic acid	P	$C_4H_4-C_6H_2 \diagdown NH$ $HO \diagup C_6H_2$ $CONH-C_6H_3-OCH_3$ CH_3	Laboratory sample	396	
o-Toluidide of 2,3-dihy-droxyanthracenecarboxylic acid	P	$C_4H_4-C_4H_2-C_6H(OH)_2CONH-C_6H_4CH_3$	Laboratory sample	343	

DESCRIPTION OF COMPOUNDS

Miscellaneous Nitrogen Compounds* (Cont'd.)

Compound	Source[c]	Formula	Description[b]	Mol. Wt.[a] Theo.	App.
2,5-Dimethoxyanilide of 2-oxydibenzofurane-3-carboxylic acid	P	C_6H_4, C_6H_2, O; HO, CONH-$C_6H_3(OCH_3)_2$	Laboratory sample	363	
p-Chloroanilide of 2-hydroxycarbazole-3-carboxylic acid		C_6H_4, C_6H_2, NH; HO, CONH-C_6H_4Cl	Laboratory sample	337	
Bis-2,4-dimethoxy-3-chloroanilide of terephthalyldiacetic acid	P	O:$CCH_2CONHC_6H_2(OCH_3)_2Cl$; C_6H_4; O:$CCH_2CONHC_6H_2(OCH_3)_2Cl$	Laboratory sample	565	
Trimethyldihydroquinoline polymer	G	[C_6H_4-C:CH-C-NH; CH_3 $(CH_3)_2$] ~3	Laboratory sample	~520	
Rhodanine	G	S-CH_2-CO-NH-CS	Laboratory sample	133	
N-Nitrosodiphenylamine	G	C_6H_5-N(NO)-C_6H_5	97% Minimum Purity[b]	198	
N-Tallow-Morpholine	AR	CH_2CH_2-O-CH_2CH_2-N-R, where R is derived from tallow	~95%[b]		341
N-Coco-Morpholine	AR	CH_2CH_2-O-CH_2CH_2-N-R, where R is derived from coco oil	~94%[b]		280
N-Phenylmorpholine	C	CH_2CH_2-O-CH_2CH_2-N-C_6H_5	Laboratory sample	163	
N-Aminopropylmorpholine	C	CH_2CH_2-O-CH_2CH_2-N-$(CH_2)_3$-NH_2	Laboratory sample	144	
Di-ß-naphthyl-p-phenylenediamine	G	$C_{10}H_7$-NH-C_6H_4-NH-$C_{10}H_7$	Laboratory sample	360	
Ammonyx CO (cetyldimethylamine oxide)	O	$CH_3(CH_2)_{15}$-N(O)-$(CH_3)_2$	20% active[b]	286	
2-Mercaptobenzimidazole	Mo	C_6H_4-N:C-NH; SH	Laboratory sample	150	
2-Allylthiobenzothiazole	Mo	C_6H_4-N:C-S; SCH_2-CH:CH_2	Laboratory sample	207	
2-Vinylthiobenzothiazole	Mo	C_6H_4-N:C-S; SCH:CH_2	Laboratory sample	193	
Hexamethylphosphoramide	Mo	$((CH_3)_2N)_3PO$	Laboratory sample	179	
The structures of the following reagents listed in ORNL-1734 have since been released for publication:					
21F75	C	C_4H_9-CH(C_2H_5)-CH_2CH_2-CH(NH_2)-CH_3	Laboratory sample	171	182
16F65	C	$(CH_3)_2CHCH_2$-CH(CH_3)-CH_2-CH(NH_2)-$CH_2CH(CH_3)_2$	Laboratory sample	185	231
21F79	C	C_5H_{11}-CH(C_2H_5)-CH_2-CH(NH_2)-$CH_2CH(CH_3)_2$	Laboratory sample	213	232
21F81	C	C_4H_9-CH(C_2H_5)-CH_2CH_2-CH(NH_2)-$CH_2CH_2CH(C_2H_5)_2$	Laboratory sample	255	271
25F25	C	$(CH_2CH_2CH_2CH_2$-CH(CH_3)-$CHCH_2-)_2NH$	Laboratory sample	237	255
17F22	C	$(CH_2$-CH(CH_3)-CH_2-C$(CH_3)_2$-$CH-)_2NH$	Laboratory sample	264	292
15F53	C	$((CH_3)_2CHCH_2$-CH-$CH_2CH(CH_3)_2)_2NH$	Laboratory sample	270	293
16F27	C	$((CH_3)_2CHCH_2$-CH(CH_3)-CH_2-CH-$CH_2CH(CH_3)_2)_2NH$	Laboratory sample	354	348

[redacted]

DESCRIPTION OF COMPOUNDS

Notes

*BON = β-Hydroxynaphthoic acid.

a) Molecular weight:

Where an indefinite formula or a mixture is listed, the "theoretical mol. wt." is an average value, either quoted by the vendor or calculated from the stated percent distribution of alkyls. The "apparent mol. wt." is a titrated acid equivalent obtained in this laboratory.

b) Information marked (b) furnished by vendor; all other values determined in this laboratory.

c) Source of Compounds:

A	Alrose Chemical Co., Providence, R. I.
ADM	A. D. Mackay, Inc., New York
AR	Armour Chemical Div., Chicago
C	Carbide and Carbon Chemicals Co., New York
CS	Commercial Solvents Co., Terre Haute, Ind.
EK	Eastman Kodak Co., Rochester, N. Y.
G	B. F. Goodrich Chemical Co., Cleveland
H	Hercules Powder Co., Wilmington, Delaware
M	Merck and Co., Rahway, N. J.
Mo	Monsanto Chemical Co., St. Louis
O	Onyx Oil and Chemical Co., Jersey City
P	Pfister Chemical Works, Ridgefield, N. J.
RH	Rohm and Haas Co., Philadelphia
OR	Oak Ridge National Laboratory

[redacted]