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Prototype Indicator Strip for Tank Ammunition

FINAL REPORT

October 31, 1993

Prepared for the
U.S. Army Armament Research, Development
and Engineering Center
Predictive Technology and Quality Evaluation Division
Picatinny Arsenal
Dover, New Jersey 07806-5000
IAG EW 40 80 10 0

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EXECUTIVE SUMMARY

The main objective of this work is to develop and test color change indicator strips for accumulation of nitroesters in the case wall which will assist the U.S. Army in evaluating the quality and safety of combustible cartridge-cased ammunition held in stockpile or deployed in the field. The scope of this work is limited to bringing the prototype indicator to the stage where it is ready for collaboration with industry.

Combustible nitrocellulose ordnance casings offer advantages of: light weight, low cost, low detectability, and quick cycling of rounds by immediate disposal. However, mechanical strength is degraded with time by the action of humidity and nitroester diffusion through the casing to adhesives. The primary development effort of this study is a means to detect nitroester migration to the crucial skive joint which binds an assortment of warhead choices to propellant casings. This work has developed a prototype colorimetric indicator strip which, when applied in a field environment, produces a purple tint proportional to casing nitroester concentration, and inversely proportional to remaining adhesive joint strength.

Prior work³ developed a three-stage reaction which produced a dye from low levels of nitroglycerine in the presence of diamine [N-(1-Naphthyl)-ethylenediamine dihydrochloride] (A), sulfonic (also "sulfanilic" in this text) acid (B), and zinc (C) reagents. Other work² determined a nominal cut-off nitroester casing concentration of 2.0% weight/weight, distinguishing between mechanically sound and suspect rounds.

This work addressed the three steps in indicator strip use:

- A suggested protocol for indicator *strip preparation* was developed. Various coatings, support reagents, and backings were examined resulting in a choice of polyethylene tape coating over separate AB- and C-impregnated cellulose punches. Various methods of punch creation and impregnation were tried resulting in stirred aqueous solutions and suspensions of AB and C, respectively. AB punching after dipping/drying expedites manufacture.
- Suggested protocols for indicator *strip application* to lab backings and field casings were developed. For longevity, C and AB punches were kept separate from preparation until time of application. After chemical stripper was applied to the alumina-polyurethane paint on casings, C and AB punches were stacked and double-tape sealed.
- A means for indicator *strip monitoring* was developed. From known time of indicator reaction, casing humidity, and indicator color, a means for field concentration determination was determined. Two schematic calibration charts were developed. Lab time-lapse photography was used to calibrate the indicator at a single level of humidity.

Excluding labor, the cost of an indicator strip is estimated at under \$0.25. Without automation, labor per strip for manufacture, application, and monitor is estimated at 1 minute, 30 to 40 minutes, and 5 minutes respectively. Application time can be cut by about 75% if a sparking tool is allowed or if multiple indicator strips are assigned to the operator. Speed of indicator reaction in a lab setting is slow, requiring a return visit for monitor after between 1.5 and 2 days. Field reactions may be only roughly half as fast. Accuracy of the indicator, determined by standard 95% confidence levels ($n=5$), is about $\pm 1.5\%$ weight/weight. Range of the indicator is at least from 0.5% to 8.0%. The indicator strip size, including the full periphery of the paint-cleared patch, is 0.5 in. \times 0.5 in. \times 0.050 in.

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ACRONYMS AND DEFINITIONS

A	N-(1-Naphthyl)-ethylenediamine dihydrochloride, $C_{12}H_{14}N_2 \cdot 2HCl \cdot CH_3OH$, or "diamine" ($M_w = 291.21$ gm/mole). A is a short hand designation for the first of 3 strip indicator reagents.
B	$H_2NC_6H_4SO_3H$, or sulfonic acid ($M_w = 173.19$ gm/mole). B is a short hand designation for the second of 3 strip indicator reagents.
C	Zn, or elemental zinc ($M_w = 65.37$ gm/mole). C is a short hand designation for the third of 3 strip indicator reagents.
CCC	Combustible cartridge casing.
DEGDN	Diethyleneglycol dinitrate. Chemical relative of NG. Major M829 propellant constituent.
DH₂O	Distilled Water ($M_w = 18$ gm/mole). Reagent solvent.
MeOH	CH_3OH , or methanol ($M_w = 32$ gm/mole). Reagent solvent.
NE	General nitroester, including NG and DEDGN.
NG	Nitroglycerine. Minor M829 propellant constituent.
Patch	Generally, the 0.5 in. × 0.5 in. area on the M829 casing which is cleared of paint, and to which the strip indicator is applied.
ppm	Parts per million.
psig	Pounds per square inch, gage.
Punch	Generally, the 0.25 in. diameter circle of backing material, nominally glass fiber filter or cellulose filter.
Strip	Refers to the entire nitroester indicator including the treated punches placed on the patch and covered with appropriate coatings.

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1. INTRODUCTION

The main objective of this work is to develop and test color change indicator strips for accumulation of nitroesters in the case wall which will assist the U.S. Army in evaluating the quality and safety of combustible cartridge-cased ammunition held in stockpile or deployed in the field. The scope of this work is limited to bringing the prototype indicator to the stage where it is ready for collaboration with industry.

The evolution of this work can be traced to:

- Griest et al², who estimated that adequate casing strength correlates with approximately 2% or lower weight/weight casing nitroester (NE) concentration. Mechanical tests discovered that the lapped skive joint adhesive, used to match M829 warheads and propellant casings, was critically degraded by nitroester (NG and DEGDN) diffusion through the casing. The nitroester migration continues with time, causing ever greater concentrations and eventual mechanical failure. Future design changes may correct the problem, perhaps by adding a nitroester-impermeable polymer coat to the inside of the casing. However, a large stockpile of M829 ammunition already exists which continues to degrade and which may need to be monitored.
- Ho et al³, who adapted reagents which, when exposed to NG, initiated a 3-step dry reaction resulting in a reddish dye on glass fiber filter paper. Backings of rather large indicator area and thickness were used. The ABC reagents were applied in a 10:10:1 molar ratio in large quantities capable of detecting low (ppm) nitroester concentrations. Large quantities of ABC reagents per unit backing area were applied by use of AB mixes and brushing of C powder. As a result, distinct but rather mottled surface color was obtained. Optimal results were achieved by commingling of AB and C on the same backing while nitroester was applied soon after reagent-to-backing preparation. In light of the findings in the present work that AB react over time with C, the optimal commingling finding may be due to the large quantities of reagents and their more immediate use.
- Griest et al², and Agourdis et al¹, who have been pursuing parallel efforts to develop a casing moisture indicator. Initial lab tests with a copper sulfate support reagent on pelletized glass fiber showed shades of green proportional to humidity. Later modifications to a common TRAMEX capacitive moisture meter (Figs. 6A or 6B) have provided a working prototype. This work presumes that quantitative measures of casing humidity will be available, if indeed casing humidity has a major impact on the progression of the 3-step nitroester indicator strip reaction and if significant variation of case wall moisture is experienced in the field.

Present nitroester indicator work is aimed at bringing indicator technology to the stage where it is ready to be turned over to industry. Technical development work supporting manufacture and application centered on 3 areas: strip coating, support reagent, and backing optimization. Process development centered on preparation, application, and monitor techniques. Evaluative work supporting strip monitor followed in characterization and calibration of the nitroester indicator.

2. STRIP MATERIAL CHOICE AND PREPARATION

2.1 COATING DEVELOPMENT

2.1.1 Coating Characteristics

An ideal coating should:

- Be inexpensive, nominally under \$0.10 per strip.
- Exhibit a high degree of optical clarity. Although undesirable, translucence or tint are acceptable as long as the underlying indicator color is evident. In such a case, calibration of coupled reagents *and* coating may have to occur and coating thickness may have to be closely controlled.
- Show good wet and dry adhesion to the support reagents, backing, and to the casing.
- Be quick and easy to use. Ideally, little equipment, preparation or dexterity should be required. Electrostatic cling and bubble entrapment are vexing concerns with strip coatings.
- Be impermeable to water entry and preferably to nitroester exit. Nitroester containment allows for a greater nitroester concentration on the observed support reagent surface and for a nitroester concentration which is closer to that of the underlying casing. A moisture barrier keeps the indicator strip and casing from precipitation and external weather effects in the field environment.
- Be safe for the soldier and for the environment. Fumes, sparks, and heat may affect the soldier directly or may ignite ordnance. Toxic materials, discarded in a field environment, may harm the ecosystem.
- Show good mechanical properties. Warping and/or brittle fracture are undesirable, while conformal flexibility is valued.
- Have good surface characteristics. Specifically, a coating should have a low, consistent thickness and show little wicking into the top surface of the support reagent which might impede diffusion and color development. Thick coatings may interfere with handling or be accidentally scraped off. Ideally, a thin coating might allow the indicator strip to remain on the casing as it is loaded and fired.

2.1.2 Coating Studies

We evaluated 12 coating candidates: water sealant, polyurethane, paraffin, polyethylene tape, Household Goop (proprietary adhesive, tetrachloroethylene solvent), 5-minute resin epoxy, heated-lamination of drawn polyethylene laminate, heated-lamination of undrawn polyethylene sheet, unheated self-adhesive polyethylene laminate, hot glue stick, superglue (cyanoacrylate ester), and spray acrylic. Criteria for evaluation were: availability and cost, adhesion, clarity, thickness control, mechanical strength, workability, moisture permeability, interfering side reactions, permeability to NE, and safety. Table 1 shows the results of these tests.

All coatings were readily available and inexpensive. Each coating was available by immediate mail order or local procurement of an established commercial brand. Per strip coating costs for each of the candidates is under \$0.01.

We were able to achieve good clarity with all coatings under optimal conditions. However, some problems were noted with: paraffin, polyurethane, superglue, and acrylic. Optical clarity of paraffin is unacceptably low, due to a tendency toward clouding or scorching, except at low, even thicknesses achieved using hot-blade smoothing. Although polyurethane tends to yellow slightly, its optical clarity is acceptable, but a colorimetric calibration would need to take into account the slight, translucent shift in tint. An improved multi-material superglue was ruled unacceptable due to its tendency toward opaque white bubbling when applied to a damp surface. Indeed, even when applied to an initially dry surface, superglue provides only a fair, rather irregular lens for reaction viewing. Acrylic, though acceptable, tends to cloud slightly.

We performed bench-scale tests to check for adhesion to (nitro)cellulose backing. With proper handling (e.g., with paraffin and hot lamination) all wetted well, so long as the surface was dry to the touch. None of the coatings adhered well to water-sodden backing, although resin epoxy and urethane provided an inferior bond as the backing dried. The only coatings which performed acceptably when applied to a dry surface and soaked overnight were polyurethane, hot glue stick and cold self-adhesive laminate.

We experienced workability problems with: Goop, drawn polyethylene, undrawn polyethylene, and hot glue stick. Goop clumping makes it unworkable for this purpose. Without careful handling and pinning of edges, drawn polyethylene tends to tear and shrivel, due to polymeric chain relaxation above the glass transition temperature (T_g) of roughly 350°F. The need for a high temperature instrument (i.e., for application and hot-blade smoothing) to reach T_g poses a safety concern for work in a NG/DEGDN-laden ordnance bunker environment. This also raises concerns about hot working of (un)drawn polyethylene and hot glue stick. Hot blade smoothing was highly controllable with hot glue stick, although unintentional drawn threads or “cobb-webs” were common. Workability comparisons rate tape over cold self-adhesive laminate: lay-down and bubble removal is somewhat better with laminate but a 1 in. tape roll is simpler to use.

We checked for impermeability to moisture by sealing a 1.5 in. square of coating-impregnated cellulose filter paper against the lip of a 1 liter bottle containing air of a known relative humidity (%RH). The mouth of the bottle was immersed for over 12 hours in water, after which the rise in %RH in the contained air was determined using a hair hygrometer. Results agreed with adhesion tests: polyurethane, hot glue stick, and tape [or cold or hot (un)drawn polyethylene] edged with hot glue stick retained low %RH levels. Glue stick %RH levels were lowest. Unthickened acrylic sprays failed to provide a water-impermeable barrier, even after multiple applications.

Table 1. Nitroester Patch Coating Test Results

Rank	Title	Cost	Clarity	Adhesion	Workability	H ₂ O Permeability	Safety	Mechanical Strength	Surface Control	NE Permeability
1	Polyethylene Tape	0	0	0	+	+	+	0	+	+
2	Cold Polyethylene Laminate	0	0	+	+	+	+	0	+	U
3	Acrylic	0	-	0	0	0	0	0	0	U
4	Polyurethane	0	-	+	0	+	0	0	0	U
5	Hot Glue Stick	0	0	+	-	+	-	+	0	+
6	Resin Epoxy	0	0	0	0	0	0	0	0	+
7	Undrawn Polyethylene Sheet	0	0	0	-	0	-	0	+	U
8	Drawn Polyethylene Sheet	0	0	0	-	0	-	0	+	U
9	Paraffin	0	-	0	0	0	-	-	0	U
10	Superglue	0	-	0	0	0	0	0	-	U
11	Goop	0	0	0	-	0	0	0	-	U
12	Water Sealant	0	0	0	0	0	0	-	0	U

Key

- + Superior Rating
- 0 Average Rating
- Inferior Rating
- U Untested

5

We observed mechanical strength qualitatively, rather than by formal testing. Water seal was too thin, even on serial applications, to provide sufficient in-plane tensile strength. Paraffin showed fracture and flaking when subject to out-of-plane loading. Hot glue stick, however, showed superior toughness and dimensional stability. Aside from these observations, all coatings showed adequate mechanical strength.

Inferior surface characteristics were noted for Goop and superglue. We achieved good thickness control with all coatings except Goop. Particularly at lower temperatures Goop tends to clump and could not be brought to an even thickness over a 1.5 in. square. However, as expected, the tapes, sheets, and laminates showed superior thickness control. Wicking into the surface of the support reagent is a problem which can be solved with thickeners for polyurethane and acrylic. However, we are not aware of an appropriate thickener for superglue or water seal.

We prioritized checks for interfering side reactions and nitroester permeability as of lower screening value. However, an obvious bias in favor of polyurethane exists, since such a coating would likely have similar characteristics to that of the aluminum/polyurethane paint applied, in practice, to the exterior of the casing. The necessity and means for removal of this paint will be examined during backing tests (Sect. 2.3.2).

In our judgement, the results of these coating tests show, in declining order, the four best candidate coating configurations:

- a) Polyethylene tape
- b) Cold laminate
- c) Thickened acrylic or polyurethane
- d) Hot glue stick

2.2 SUPPORT REAGENT DEVELOPMENT

2.2.1 Support Reagent Characteristics

Ideal support reagents should:

- Exhibit a robust colorimetric response. The ideal indicator should undergo maximal color change over a nitroester (NG or DEGDN) concentration range of roughly 0.1% to 8.0% (weight/weight).
- Enhance indicator accuracy by showing minimal color variance. The indicator should undergo no reaction with coating, backing, or casing. Reagents should also not react amongst themselves. Color should be homogenous across the strip at all stages of reaction with nitroester so that a uniform color is seen at times.

Development of the support reagents is unusual, however, in that for this work the reagents were predetermined. Cost and thickness were not major concerns since material costs were already known and reagents in all anticipated placement configurations were of negligible

thickness compared to coatings and backing. The major concerns with support reagent development was the optimal amount of each reagent, and the best preparation and application method.

2.2.2 Support Reagent Studies

In our studies of support reagents, we considered or employed various methods of reagent application including: dipping in an aqueous or ethanol mix or solution of reagents, rubbing on or applying reagents with a brush, and vacuum suction through a backing or exact volumetric spotting of reagents.

Robust Response

We looked toward maximum colorimetric change in a range centered about 2.0% nitroester concentration (weight/weight) and with limits extending to about 0.1% and 8.0%. Further, we looked for limiting interference, or colorimetric variation unrelated to NE concentration.

Although the Griess reaction² is irreversible, given sufficient time all but the lowest NE concentrations show a complete colorimetric progression from white through deeper shades of purple-pink to a final state of red (in aqueous) or a slightly mottled purple (on glass fiber or cellulose filter paper). At a defined elapsed time from start of the reaction, the changing color can be viewed and related to an partly calibrated chart.

A major difficulty with centering the colorimetric change in the prescribed range lies in adjusting the rate of color change to allow time for color viewing. Reaction accelerators such as moisture and zinc can allow less time for the viewer to cross reference the observed color to a color/concentration chart. A time to completion between many hours and a few days would probably be acceptable and show little color variation over the few minutes needed by an inspector for color determination.

From previous work, it was anticipated that moisture would speed the Griess reaction. Indeed, it was for this reason that coating impermeability to moisture was adopted as a major criteria so that variations in bunker moisture should not add variability to indicator readings. Initial tests and preliminary problem investigations (e.g., zinc effects) were conducted in aqueous solution to speed the reaction to a period under a minute. Later tests on sodden backing showed complete reaction in times under 8 hours and "dry" (about 30%RH) reaction times over 2 days. Large variations in the humidity in the casings will affect patch reaction time and require calibration of final patch "recipe" for concentration vs time vs humidity. Such humidity measure would, presumably, be available from prototype moisture indicator work. Alternatively, a subcoat between patch and casing, and permeable to NE and impermeable to water, would have to be found. Rejection of casing humidity variation by this means seems unlikely since neither the existing alumina/polyurethane paint nor any studied coatings show these coupled characteristics.

Zinc, as grey catalyst to the first of 3 reactions which produce dye from NE, regulates the rate of indicator colorimetric progression. One major reason for keeping the amount of zinc low is grey color of zinc can overwhelm the delicate colorimetric changes of the Griess reaction. This problem with zinc greying was effectively solved by keeping zinc on a separate punch, set below the punch containing the other 2 reagents. Zinc's grey color was thereby kept away from the viewing surface.

Variance Reduction

The second reason for keeping the amount of zinc low is that, in theory, increasing amounts of catalyst zinc should speed up the reaction, possibly even allowing little time for viewing an ever changing color. Prior work had set the molar ratio of zinc at 1/10th that of the other 2 indicator reagents. We found expected increases in Zn/punch retention when dipped in aqueous suspensions containing more zinc (Fig. 1). However, we found that fairly large variations in the rather high levels of zinc (1 to 10mg/ml distilled H₂O) showed little effect on reaction progression. We also found that in this range, reaction progression was sufficiently slow to reduce errors due to exact timing of placement and monitor of punches. Therefore, we chose a value (2.3mg/ml DH₂O) midway in the color-insensitive range. This, then, provides the advantage that slight variations in the amount of zinc per punch should not affect measurement variance.

We have not been successful, however, in our attempts to introduce high concentrations of AB to punches which, in theory, should reduce variability by making for nearly immediate reaction with any NE molecules regardless of variability in amounts of AB. Therefore, at high AB levels, only NE concentration differences would affect colorimetric variation. Our problem started from a desire to use a solution of AB to give even deposition and a homogenous, easily-read surface color. However, we were constrained by the solubility limits of AB (discussed below). Multiple dipping-and-drying, which we termed "waxing," is an obvious way to build up more reagent on punches while still using solutions. However, our initial tests showed that double and triple dipping created greyish punches with blackish "furred" edges. Apparently, lateral wicking to the edge of the punches may be depositing slightly more reagent there. However, the overriding concern is the greyish discoloration of the punches during waxing which reduces their value for use in a colorimetric indicator. We believe that this issue deserves further investigation and that waxing still holds promise.

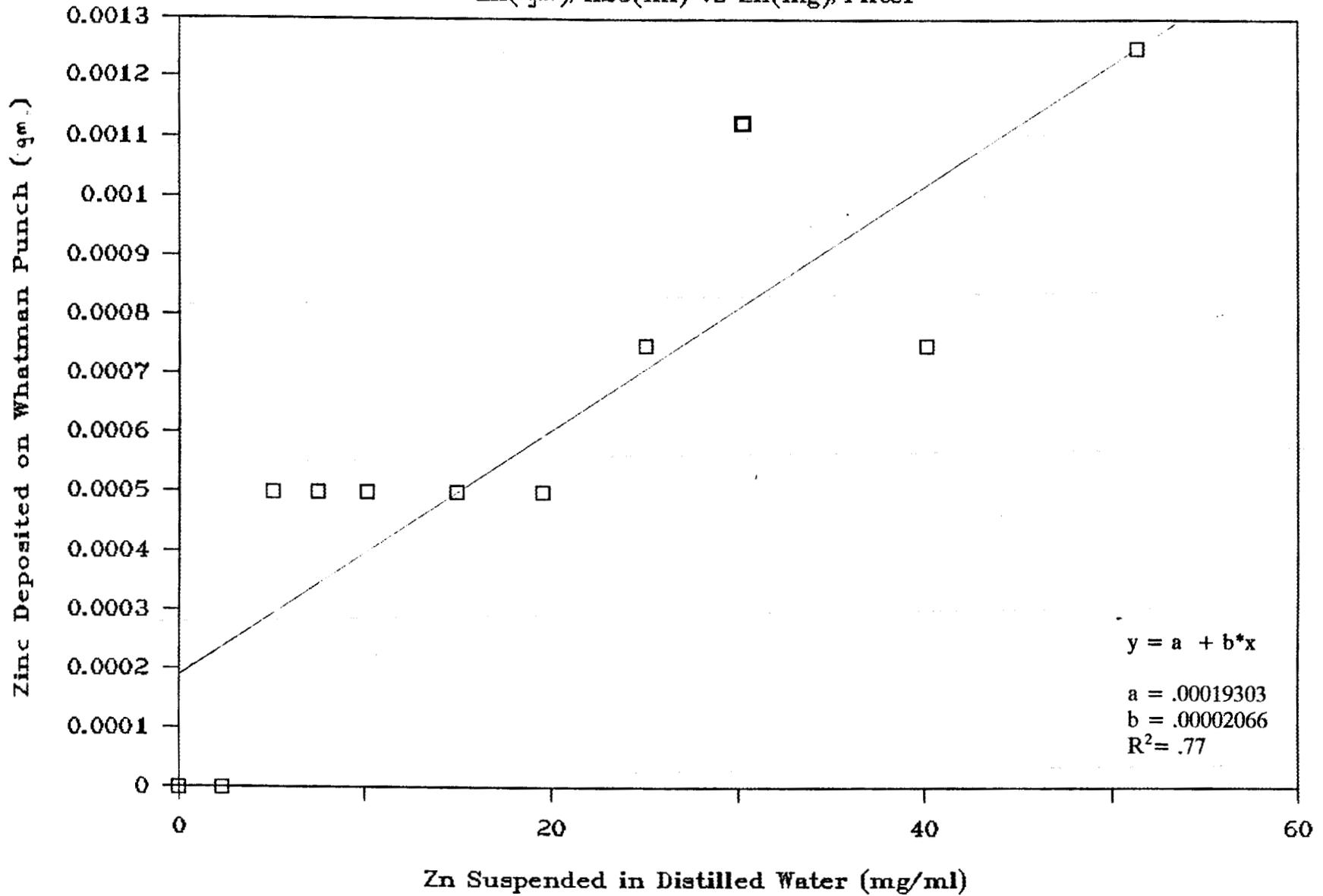
We found other sources of variability including: moisture, which accelerates the reaction; and zinc, which appears to cause a reaction *amongst* the indicator reagents and with the indicator dye, irregularities in amount and preparation of reagents, and irregularities in application of prepared reagents to the backing surface.

Zinc-induced variability is partly derived from the metal's high reactivity. First, zinc reacts with the other indicator reagents even in the absence of NE. In a creamy aqueous suspension of the indicator, a metallic spongy nodular precipitate was seen in minutes. In a covered, pulverized-solid mix, significant loss of reactivity was noted in 5 days; and although no precipitate was detected, addition of zinc appeared to "revitalized" the indicator mix. The heavy, metallic nature of the precipitate and zinc revitalization suggest that a reaction amongst the 3 indicator reagents with a high zinc content occurs, preventing the Griess reaction. Second, zinc appears to react with the red dye formed from the Griess reaction forming a grayish precipitate and removing color from an aqueous solution or the center of an indicator patch. The remaining fluid or solid may take on a yellowish or brownish hue. It appears that zinc should be kept separate from the other 2 reagents until the time of casing test. Surprisingly, there is evidence that zinc in aqueous reacts with each of the 2 indicator reagents, so the apparent solution is to prepare a backing containing the diamine and sulfonic acid separately from the zinc.

Zinc-induced variability is also derived from the metal's insolubility in, and high density relative to, water or methanol. Even though only fine particles which pass a 50 grate were used, constant stirring is needed to maintain a suspension. Even a high volume suspension

Fig 1. Suspended Zinc Retention

Zn(gm)/H2O(ml) vs Zn(mg)/Filter



spotted to filter paper does not spread evenly. Rubbing or brushing with zinc, as suggested by prior work, provides good dispersion, although microscope inspection shows some unevenness in distribution in each case: rubbing preferentially fills the pits while brushing shows slightly more zinc particles on the surface fibers. Dipping of the backing into a well-stirred aqueous suspension of zinc provides good dispersion and even distribution.

We gave up quicker MeOH evaporation for greater safety and solubility with DH_2O , since solubility was the key to clear homogenous indicator color. We attempted use of powdered mixes, slurry suspensions, and solutions of the 3 indicator reagents to determine the means for patch preparation that provided greatest control of indicator deposition per unit patch area. We were predisposed, however, toward dipping of a backing in a stirred solution of methanol and the 2 soluble indicator reagents (i.e., the diamine and sulfonic acid). This provided an even volumetric deposition on the backing without clumps. Neither A nor B reagent, however, showed high solubility in methanol and the amount of methanol required might force numerous indicator solution spikes to deposit sufficiently large amounts of (>4:1 molar ratio to NE) so that variance due to weighing and transfer errors in the 2 soluble indicator reagents was reduced. Both A and B reagents are much more soluble in distilled water: the solubility of the diamine and sulfonic acid in distilled water is about 35 mg/ml and 20 mg/ml respectively.

A loose-knit, double-polyurethane-coated, mild steel grate support was used to reduce indicator capillary flow to, and loss on, the supporting petri dish. The polyurethane coats on the grate were applied to avoid unintended reaction of indicator reagents with the grate materials. Indeed, initial use of uncoated copper proved unsatisfactory since diamine/sulfonic acid-dipped filter punches turned black whether applied wet (in 1 hour) or dry (overnight). Later attempts to use a galvanized grating double-coated with polyurethane appeared to show scattered reaction of the zinc galvanization at cracks in the polyurethane coat. Local reddish-grey discoloration results, often in the pattern of the grating in the vicinity. The same grating locations show similar discoloration on subsequent trials. Such reaction is undesirable since discoloration distorts colorimetric readings and galvanized zinc reaction with AB reagents in the filter alters and reduces the amount of AB available for nitroester dye formation.

2.3 BACKING DEVELOPMENT

2.3.1 Backing Characteristics

Ideal backing should:

- Be inexpensive, nominally under \$0.10 per strip.
- Be of a homogenous, white color.
- Be easily affixed to the casing. Adhesive compatibility with the coating is also important.
- Undergo no reaction with nitroester, indicator reagents, or air.
- Be thin, to avoid accidental removal and to allow for M829 round firing without strip removal.

- Show little or no change in shape due to humidity or mechanical handling. Little or no swelling (e.g., with humidity) should exist, for this may add to variance by increasing the volume for nitroester diffusion. Stretching or compression by handling may have a similar effect.
- Exhibit high permeability to nitroester diffusion, to allow nitroester migration from the casing to the observed surface of the strip.
- Show good mechanical properties. The ideal backing should maintain its form while showing enough flexibility to conform to the cylindrical casing.

2.3.2 Backing Studies

We have looked at various backing media: nitrocellulose casing, glass sphere pellets, starch pellets, Varian/3M polymeric filter, glass fiber filter and cellulose filter. We have performed adhesion and stripping tests on cardboard proxy and actual casing. To date, however, nitrocellulose casings have been in short supply and so have not been fully tested.

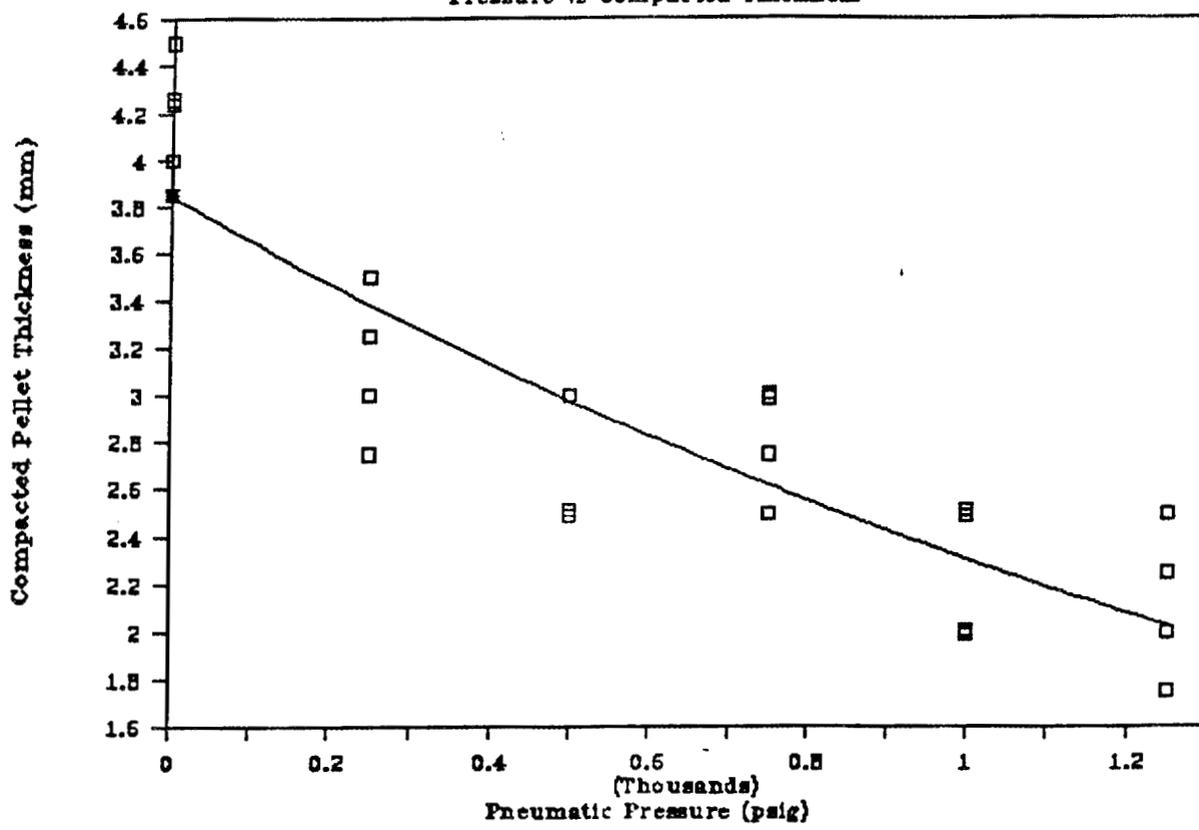
Though the possibility of avoiding patch application is attractive, direct indicator mix "painting" of casings is complicated by varying degrees of casing moisture content, possibly affecting paint adhesion, paint penetration into the casing, and previously observed yellowing of the casing.

Pellets of glass spheres or starch are attractive because pellet characteristics can be controlled by addition of indicator reagents before pelletization and by variation of pelletization pressure. Pelletization was accomplished using a pneumatic cylinder, pedestal, and plunger apparatus. Both glass sphere and starch required a binder to facilitate pelletization. Distilled water was chosen because post-pelletization evaporation was found to remove most of the water without, in most cases, significant crumbling or loss of pellet cohesion. Further, the complication to NE diffusion of voids filled with a persistent binder was avoided by simple post-pelletization evaporation. Glass sphere pellets, though not prone to yellowing, showed inferior cohesion at any tested levels of pressures (0 to 1250 psig) or amount of water binder (0 to 0.6 ml/mg). Starch pellets showed best pelletization between 500 and 750 psig (Fig. 2). Lower pressures (0 to 500 psig) showed crumbling on drying while higher pressures (750 to 1250 psig) tended to cause binding of the plunger apparatus. We believe plunger binding may be due to elastic compaction of the starch in the cylinder; if so, higher working pressures may be more easily obtained if care is taken in design to avoid any plunger eccentricity. Interestingly, below 750 psig, pellet compaction did not appear to occur by compression or strain of the cellulose particles. Microscopic (3X, 10X, 40X) surface examination showed that the compaction mechanism was macro-void or fissure closure up to about 750 psig.

Figure 2 shows the effect of compaction on starch, with an exponential fit shown in the solid line. The fit falls outside the 4 data points at 0 psig, yet it nearly matches the 0.16 in. (4 mm) initial thickness of the cylindrical pellet. We believe the reason lies in the swelling of starch on initial addition of binding water which is seen to be squeezed out between the plunger and cylinder walls at low pressures (~ 250 psig).

Fig. 2: Pelletization of Starch

Pressure vs Compacted Thickness



Despite the fairly regular data from compaction, we feel that pelletization is troublesome. Large pellet volumes may, perhaps unnecessarily, complicate the re-equilibrium of diffusing NE and the estimation of casing concentrations. Thick pellets may show substantial edge effects on diffusion, causing radial color variations. Thick pellets will protrude from the casing. Thick and/or hard pellets may create difficulties in attachment to the cylindrically curved casing. Top surface spiking with indicator solution tends to degrade the pellets' cohesive strength. These problems could be addressed by making small, thin pellets; by combining the 2 non-metallic binders with a water-binder at time of pellet formation; and by applying the zinc coating by a dry method (e.g., rubbing or brushing) at time of indicator patch application to casing.

The greatest difference noted between the cellulose and glass fiber filter paper we have examined has been pore size, thickness and compressibility, and whiteness. The cellulose paper has larger pore size, while the glass fiber paper was thicker, whiter (and less likely to yellow with sulfonic acid) and showed a "spongy" damped-elastic compressibility. The thin, loose-fibered Whatman cellulose filters retain less moisture but also less indicator solution. An advantage is that they dry more quickly, making patch preparation easier, particularly in the event of serial indicator spots or waxing. Lower compressibility is also an advantage since operator technique will be less likely to affect thickness and internal void volume of the patch (i.e., pore size affecting NE diffusion).

An alternate backing candidate and punch processing technique yields marginal results. Varian/3M Empore polymeric filters (i.e., styrene - divinyl benzene in teflon fibril network) can be impregnated with standard aqueous AB solution under varying levels of vacuum. Varian filters show problems related to thickness and punch deformation, as well as poor surface color development over time when exposed to NG. Vacuum-induced impregnation is uneven. Low impregnation at points of ceramic support are indicated by low local color change. Unsupported areas of the filter showed greater color change, presumably as a result of greater impregnation due to greater locally applied vacuum.

2.4 PREFERRED PROTOCOL FOR STRIP PREPARATION

By present best practice, A and B reagents are placed on the same punch backing, as shown in Fig. 3. A virgin 11 cm diameter Whatman cellulose circle is dipped once, using tweezers, in a stirred aqueous solution of the diamine and sulfonic acid (1:1 molar ratio). The AB-treated cellulose circle is placed on a double-polyurethane-coated mild steel grate and air-dried for a nominal period of 2 to 3 hours (75°F, 40%RH). Latex gloves and a common nickel-coated 0.25 in. diameter hole punch are used to create the finished AB punches with a deposition of about 0.5 mg of AB per punch. Dry AB-treated punches are collected and covered, nominally in petri dishes marked with date and lot of preparation.

By present best practice, C reagent is supported on a separate punch backing as shown in Fig. 4. Using latex gloves and a common nickel-coated 0.25 in. diameter hole punch, a virgin 11 cm diameter Whatman cellulose circle is punched. Using tweezers, each punch is dipped once in a stirred aqueous suspension of zinc powder (200 mesh; 2.3 mg/ml) for a deposition of about 0.6 mg/punch. The C-treated punches are placed on a double-polyurethane-coated mild steel grate and air-dried for a nominal period of 2 to 3 hours (75°F, 40%RH). Dry C-treated punches are collected and covered nominally in petri dishes marked with date and lot of preparation.

Fig. 3. Organic Reagent Punch Preparation

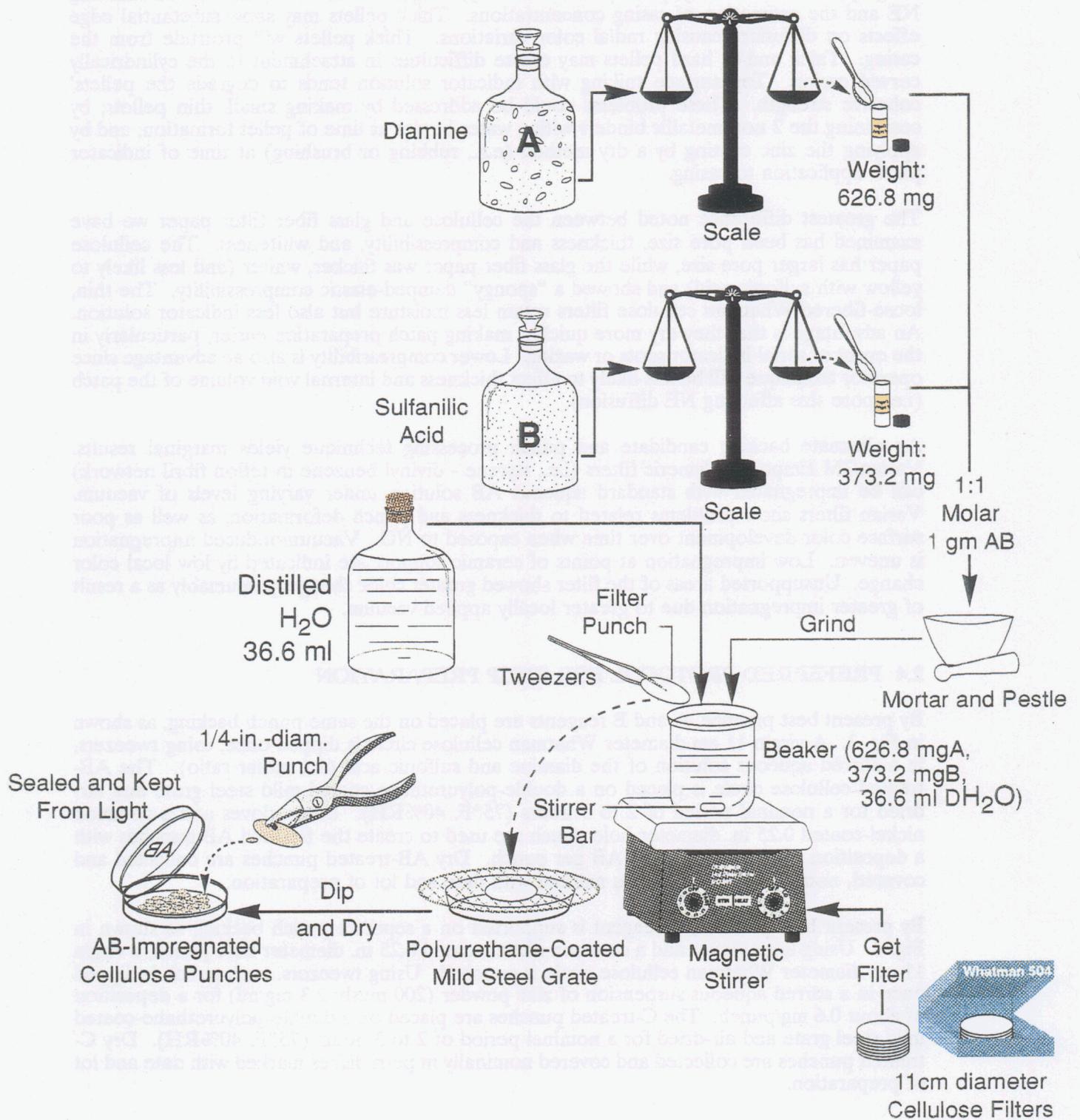
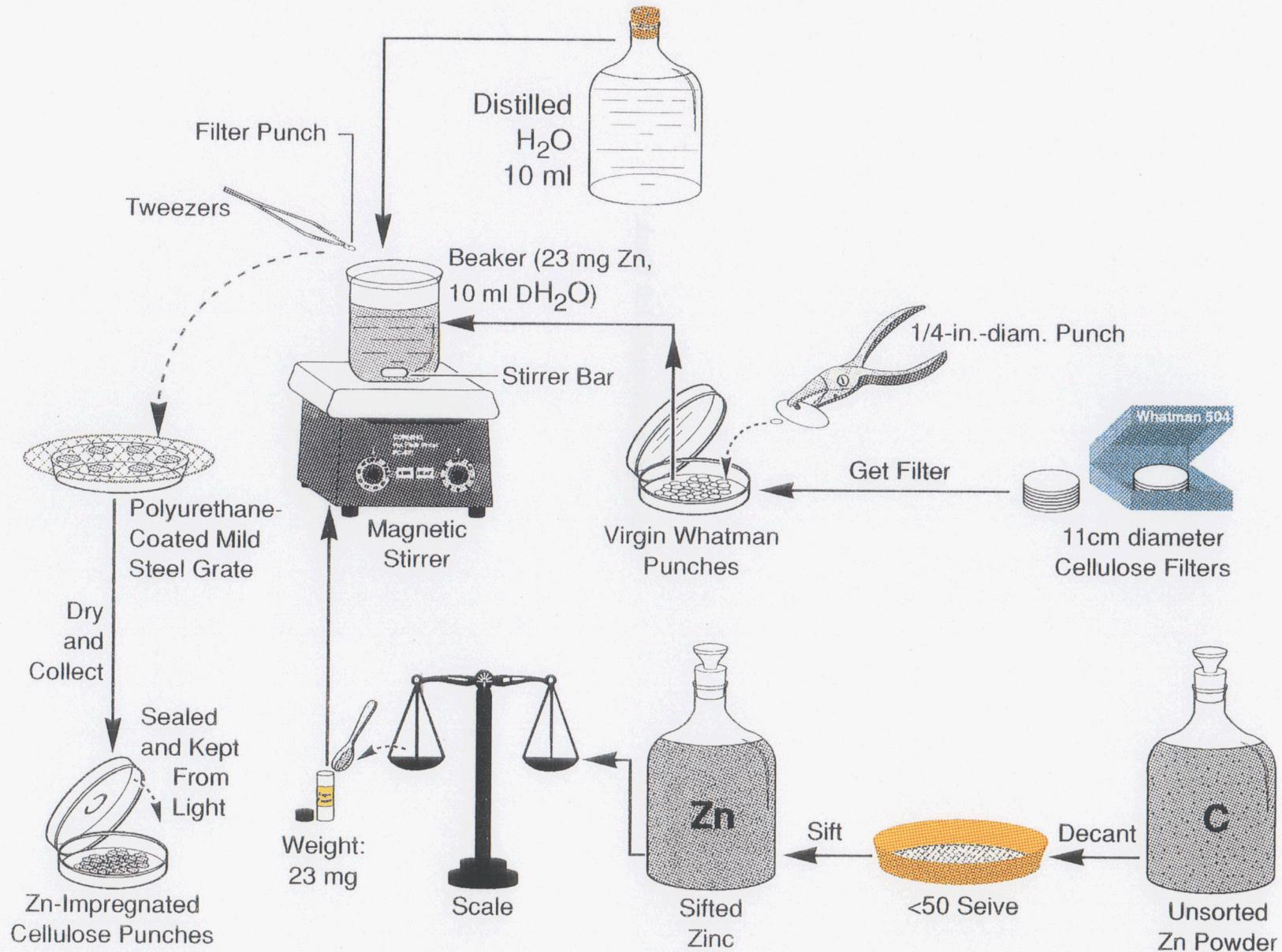


Fig. 4. Zinc Punch Preparation



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3. STRIP APPLICATION

3.1 CASING PREPARATION DEVELOPMENT

As seen in Fig. 1, the leading candidates for coatings (polyethylene tape, cold laminate, polyurethane, and acrylic) show little or no permeability to NE. This is a positive characteristic for coating but it means that the aluminum-polyurethane paint on the M829 casings must be removed at the site of patch application. Two options were studied: mechanical abrasion and chemical degradation.

Mechanical abrasion was accomplished using a sander drum mounted on a cordless Dremel Mini-mite against a 1.5 in. × 1.5 in. cellulose square coated with polyurethane. Squares were cleared in under 30 seconds removing an average of just under 0.5 mil or an average of 12 mg/cm². Unfortunately, such tools are abrasive and most are not brushless. External and internal sparking and power dissipation may pose an unacceptable risk to operation in an ordnance bunker.

Chemical degradation was achieved by 2 coats (~0.5 ml each) of urethane lacquer thinner. This non-flammable agent wrinkled the surface of the aluminum-urethane paint on a 0.5 in. × 0.5 in. sample. After the vendor-suggested 10 minutes, this paint was easily removed as a sheet and a second coat of thinner was applied. After a similar time period, the remaining metallic paint was scraped from the casing surface. This casing was then allowed to dry for 5 minutes. Microscopic (3X) examination showed no apparent nitrocellulose degradation or absorption of the viscous lacquer, but some patches of metallic paint remained which required surface cleaning/drying and possible light sanding by hand.

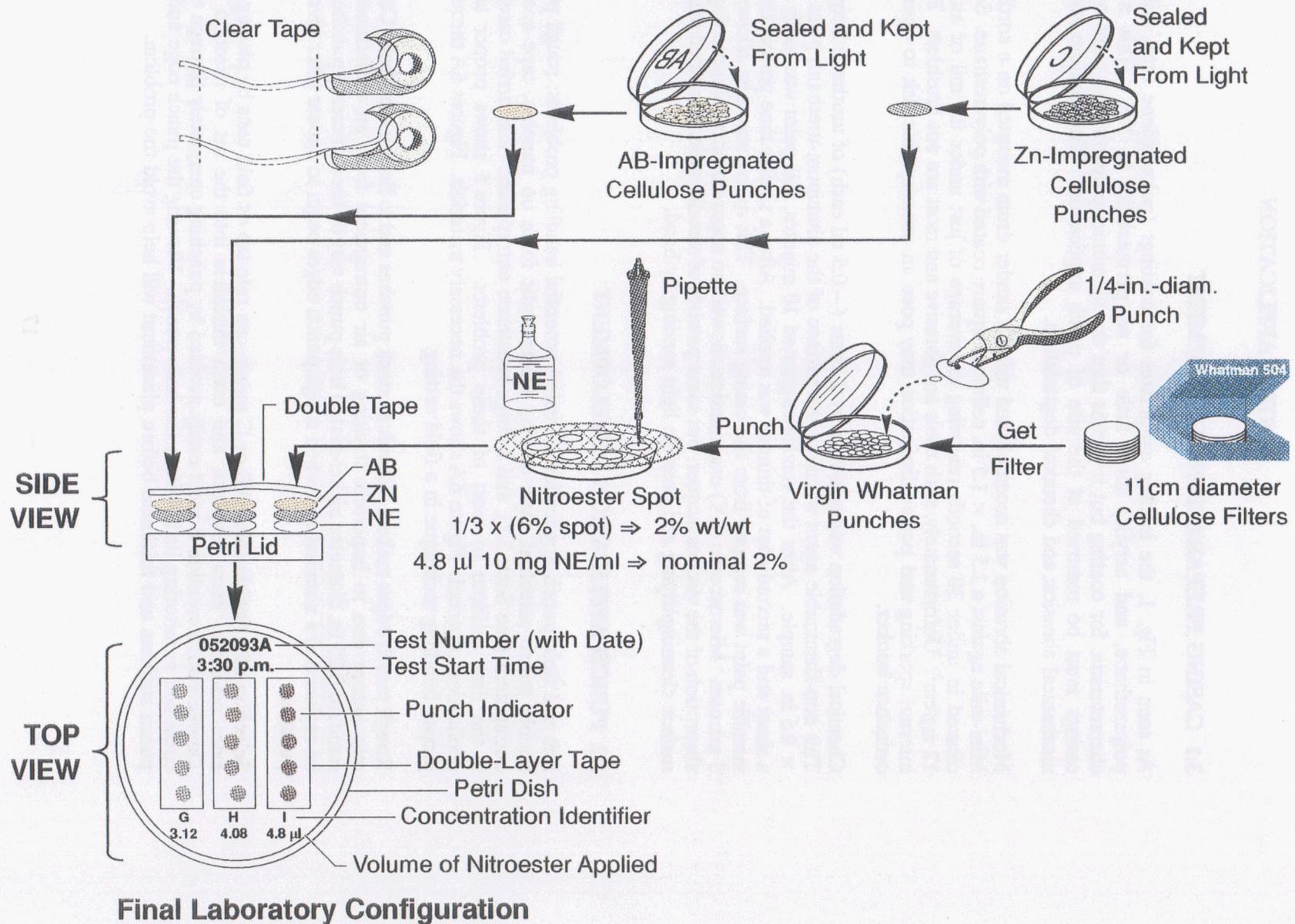
3.2 PUNCH APPLICATION DEVELOPMENT

Lab and field punch application revealed potential handling problems: rough punch edges, double punch selection, tape coating electrostatic force on punches, tape coating bubble entrapment (see Sect. 2.1), and foreign substance entrapment. Unhurried careful handling is the first antidote to most of these problems. Figure 5 shows proper lab indicator application protocol. Figure 6A shows the necessary materials. Figures 6A through 6K show proper handling technique in a field setting.

Rough punch edges make it difficult to stack punches and to flatten the stack. Color variance may accrue due to imperfect stacking or air entrapment from an unflattened stack. A standard 0.25 in. diameter nickel-plated hole punch may be used to create punches but should be replaced at a nominal cost when rough punch edges begin to appear after several hundred punches.

Selection of a double-thick AB or C punch can ruin lab or field tests by placing unexpected extra cellulose, extra reagents, and extra thickness into the set of reaction parameters. Double punch creation is most easily avoided by punching completely through the cellulose circle and monitoring its fall from the hole punch. Viewing the punch edge and monitoring punch stiffness and thickness before placement will help avoid the problem.

Fig. 5. Laboratory Indicator Application



Tape coatings may apply an electrostatic force which can disrupt stacked punches. This problem is simply solved by holding the stack in place with a probe until the edge of the stack has been secured by the tape.

Bubble entrapment often results from tape placement over a punch which protrudes from the casing surface. The trapped air affects lab test variance most by increasing the reaction volume. Lab and field test coating adhesion is affected since the area of coating contact to the casing is reduced. Further, it is possible to create a wrinkle through which the external environment (especially humidity) may affect the entire strip. To avoid air entrapment, 2 layers of tape are applied, as shown in Figs. 6F and 6H. The first layer is applied mainly to hold the punches in place. It is scored lightly with a razor to create a slit (Fig. 6G). Entrapped air is evacuated through this slit using a probe which is pushed around the punch perimeter. A second layer of tape is then applied to make the seal.

Humidity, skin oils, dirt, or camouflage stick may be carried from the hands onto the punches with various effects on indicator strip error. We found a good balance between cleanliness and dexterity is reached by placing only one hand in a latex glove. This gloved hand is used for all strip surface contact. It also provides a measure of personal protection against the polyurethane stripper.

3.3 PREFERRED PROTOCOL FOR FIELD STRIP APPLICATION

The casing application area is marked and constrained to 0.5 in. \times 0.5 in. by a border of 1 in.-wide masking tape (Fig. 6B). The casing surface is prepared by 2 serial applications of polyurethane lacquer thinner (10 minutes apart) (Fig. 6C); each application is followed by a light scraping and wiping (Fig. 6D). Stripper residue is allowed to dry for 5 minutes and a casing relative humidity reading is taken and recorded. If necessary, a light sanding is applied and the surface is again wiped clean. The zinc (C) punch is laid on top of the cleared nitrocellulose casing with the surface which rested against the grate down (Fig. 6E); consistency in this practice will help reduce indicator variance. The diamine-sulfonic acid (AB) punch is placed on top of the C punch. A first 2 in. \times 1 in. piece of polyethylene tape is applied (Fig. 6F). This tape is lightly scored with a razor and any air is removed by tracking the punch perimeter with a probe (Fig. 6G). Then, another 2 in. \times 1 in. piece of polyethylene tape is applied to seal the punches (Fig. 6H). A tabbed 1 in. \times 2 in. strip of foil tape with light adhesive may be applied in the perpendicular direction to form an "X" design. Foil tape application, though not strictly required, is of good practice since the colorimetric reaction is only slightly light sensitive. Date and time of application is recorded (Fig. 6I).



Fig. 6A. Materials for Field Application and Monitor of Strip Indicator.



Fig. 6B. Masking Tape Border and Casing %RH.

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Fig. 6C. Paint Stripper Application.

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Fig. 6D. Paint Removal: Scrape and Wipe.

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Fig. 6E. Punch Lav Up.

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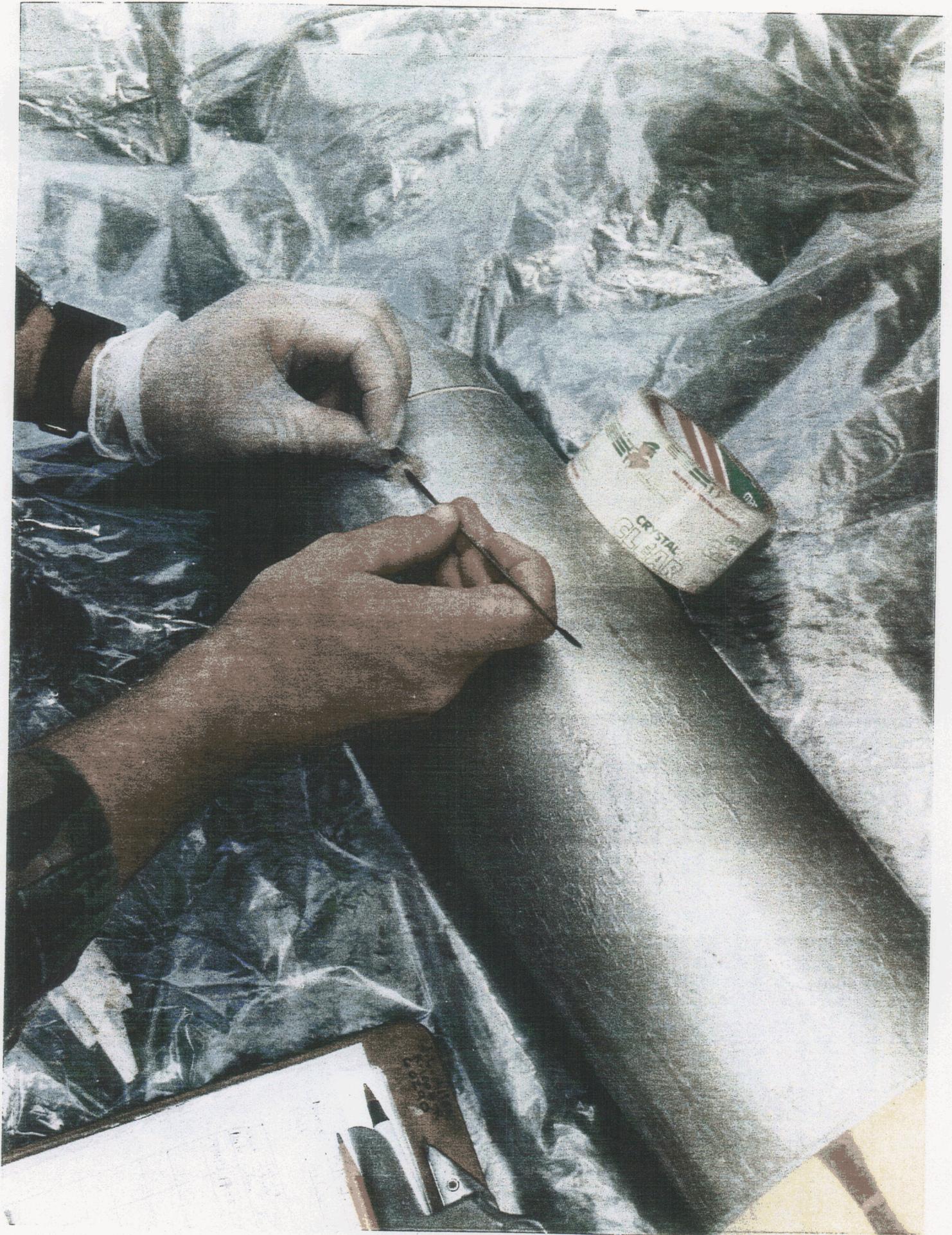


Fig. 6F. First Taping.

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Fig. 6G. Scoring of Tape.

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Fig. 6H. Second Taping.

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Fig. 6I. Record of Application Data.

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4. STRIP MONITOR

4.1 CALIBRATION

A full calibration trial protocol (Fig. 5) was developed to include 75 samples: 5 samples at each of 15 nitroester concentration levels between 0.1% and 8.0% weight/weight (Figs. 10A and 10B). The 5 samples per concentration level provided a variance estimate, while 15 spaced concentration levels around the 2.0% acceptance criterion charted the effects of concentration. Time lapse (5 minutes between 1 to 2 second viewings) provided a record of colorimetric change with time. All trials described below were performed using a known NG/DEGDN-spiked cellulose filter as the nitroester source applied on clear plastic backing (e.g., a petri dish lid). Larger volumes were placed by serial spots of no greater than 2.4 ul (10mg/ml MeOH), a volume determined to fill the filter punch volume. The bottom cellulose punch was triple-spiked with the appropriate nitroester (10mg/ml MeOH). The middle punch was zinc-slurry dipped (23mg Zn/10ml DH₂O). The top punch was dipped in AB solution (1:1 molar AB; 147mg AB/5.25ml DH₂O). Tape-sealed samples were left in the overhead camcorder's field of view for up to 3 weeks. Light sensitivity was determined to be minimal at 200 lux (note: mid-day sun is typically 5,000 to 50,000 lux) and calibration was performed at under 200 lux of continuous lighting.

Visual qualitative spot monitor was supplemented by detailed quantitative analysis of data derived under the following conditions:

- Standard NG spikes. Qualitative observations show expected color progression with time and concentration (across the entire 0.1 to 8.0% range) but lower concentrations effectively stall at mid-color change and show higher variability presumably due to spot volume variability. (See Appendix).
- DEGDN spikes. No apparent difference between DEGDN and NG color progression was noted by visual inspection.
- Predipped AB filters to replace the standard post-dipped filters. Motivation was that five-fold processing step speed-up can be accomplished if method showed satisfactory colorimetric progression. Qualitative observations are promising.
- NG-spiked AB punches. Unspiked virgin Whatman cellulose was placed as the bottom layer. This test has value in discounting direct "painting" of the casing because of observed dark, rapid, and variable surface color progression through shades of purple to a final red-brown.

4.2 CHARACTERIZATION

After choices of best coating/reagent/backing are settled, a final characterization of the patch as a rough sensor or indicator should be made according to: cost (\$/patch), size (minimum volume), speed (time constant), range (maximum and minimum %NE), and accuracy (including indicator variability and cognition factors). The Appendix expands on issues of speed, range, and accuracy.

Materials Cost:	<\$0.25/strip
Preparation Labor Cost:	1 minute
Application Labor Cost:	30 to 40 minutes
Monitor Labor Cost:	5 minutes
Size:	0.5 in. × 0.5 in. square patch 0.25 in. diameter circle < 0.050 in. thick
Speed of Viewing:	1.5 to 2 days until viewing
Speed of Reaction:	18.7 hours time constant
Range:	0.5% to 8.0% weight/weight
Precision:	± 1.5% (for n=5, 95% confidence) Higher errors at low concentrations
Resolution:	33% cyan variation at specified range and view window

Direct NG spikes to AB filters showed quicker but poorer color progression. Rings of color indicate little lateral NG progression and the quick but mottled color development are presumed due to reaction acceleration by moisture and possible Zn-AB reagent side reactions. This implies that painting of cleaned casing surface is probably not a good idea for similar reasons.

AB solution degradation with respect to time to an opaque brown was verified in a sealed capsule and time-lapse recorded.

Time Studies

Lab time studies of filter preparation showed that dipping, then punching, is far quicker, though more wasteful of reagents. Dipping a prepunched filter in stirred AB solution takes 7 to 8 seconds, while dipping an entire filter prior to punching takes 1 to 2 seconds. About 2 seconds per punch is required for manual punching, while about 30 minutes is required for either AB or C (Zn) aqueous preparation (e.g., gathering and cleaning of glassware and for reagent weighing, grinding, and mixing) which can serve many hundreds of punches.

Dipping in AB solution before drying and subsequent punching appears to be a promising change to the protocol for filter preparation. Although some loss of AB reagents is seen by dipping first, due to lost area from punching of about 32%, postdipped punches are less white due to lateral wicking of sulfonic acid, which causes a yellowish tint on the outer 0.25 in. The reason for the slight yellowing of the entire postdipped punches is due to this edge-effect including the entirety of the 0.25 in. diameter punch. However, some minor warping of the entire predipped filter is noted prior to punching, but no apparent flaking or difficulty with punching occurs. Predipped punching is also preferred as it requires less dexterity and could more easily be automated on a large scale. Qualitatively, predipped punches show little or

no apparent difference in color progression from postdipped punches. This crucial factor has been quantified by parallel time-lapse studies of both techniques discussed under Sect. 4.1, "Calibration."

Time studies of casing application show that it takes about 30 to 40 minutes to apply an indicator to an unprepared casing. This includes: 2 to 5 minutes of set up, 10 to 12 minutes for each of 2 stripper applications, 5 minutes for stripper wiping and drying, 1 to 2 minutes to apply both filters (C and AB) indicator, and 2 to 4 minutes for documentation and cleanup. Note that about 3/4 (73-83%) of the application time is spent on activities related to chemical stripping of the preexisting alumina-polyurethane paint. Since only 1 to 2 minutes would be required for Dremel abrasive patch removal (vs 25 to 29 minutes for chemical removal), a rough 75% time savings could be achieved if munition ignition by electrical dissipation or abrasive sparking is ruled as acceptably remote. This would cut total casing application time to roughly 6 to 13 minutes. Unless the Army feels mechanical abrasion is acceptable, we will report chemical paint stripping as the preferred protocol path.

4.3 PREFERRED PROTOCOL FOR CASING MONITOR

After a prescribed period, the optional foil cover is carefully peeled back far enough and long enough to allow for a colorimetric reading. Only 1 leg of the tape-foil "X" design should need to be lifted and a hand should be placed on the other 3 legs of the "X" to maintain indicator integrity. Using the calibration chart and a light (if necessary), a reading is taken (Fig. 6J) and recorded (Fig. 6K). The foil is then immediately replaced over the indicator and the chart may be read for NE concentration as a function of relative humidity (i.e., at application), time, and color.

Figure 7 shows a color decomposition chart from which a numerical color reading (e.g., "Cyan 18.6%") can be taken in a field setting and reviewed later by the quansus. Alternatively, direct field %NE determination can be made from a calibration chart. Figures 8 and 9 show a schematic calibration chart and how it may be read for NE concentration. In Fig. 9, three variable values are used to enter the chart: a humidity of 20%RH, a time of 1.75 days, and a color index of 18.6% cyan ("geisha"). Humidity and time produce a reaction progression (equivalent time at 15%RH) of 4.3 days. Reaction progression and color then produce an intersection at 2.0%NE. This reading would then be submitted for superior's attention since NE concentrations at or over 2.0% (weight/weight) should be flagged as of suspect adhesive strength.

If the patch needs to be removed, then all 4 legs of the patch "X" design should be peeled back and the patch pulled away. The 4 legs can then be folded over behind the filters to contain the NE-impregnated waste. The 0.5 in. diameter circle of exposed nitrocellulose can then be repainted with an approved alumina-polyurethane paint.

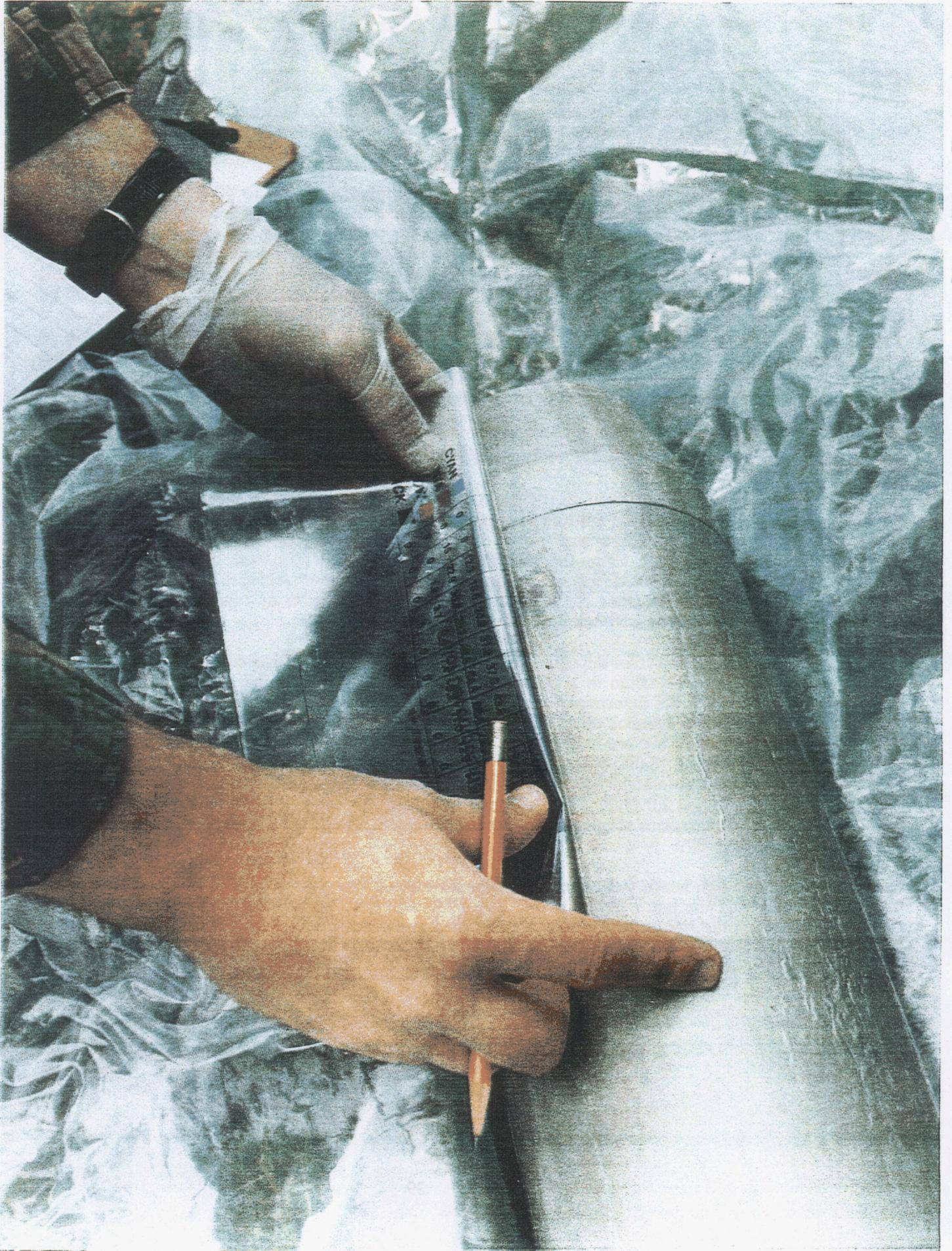


Fig. 6J. Color Index Determination.



Fig. 6K. Record of Monitor Data.

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CYAN 	0	6	12.3	18.6	24.9	31.2	37.5	43.8	50.1	56.4	62.7	69
MAGENTA 	0	15	22.9	30.8	28.7	46.6	54.5	62.4	70.3	78.2	86.1	94
YELLOW 	0	0	1.8	3.7	5.5	7.4	9.2	11.0	12.9	14.8	16.6	18
BLACK 	0	0	0	0	0	0	0	0	0	0	0	0

Fig. 7. Nitroester strip color decomposition.

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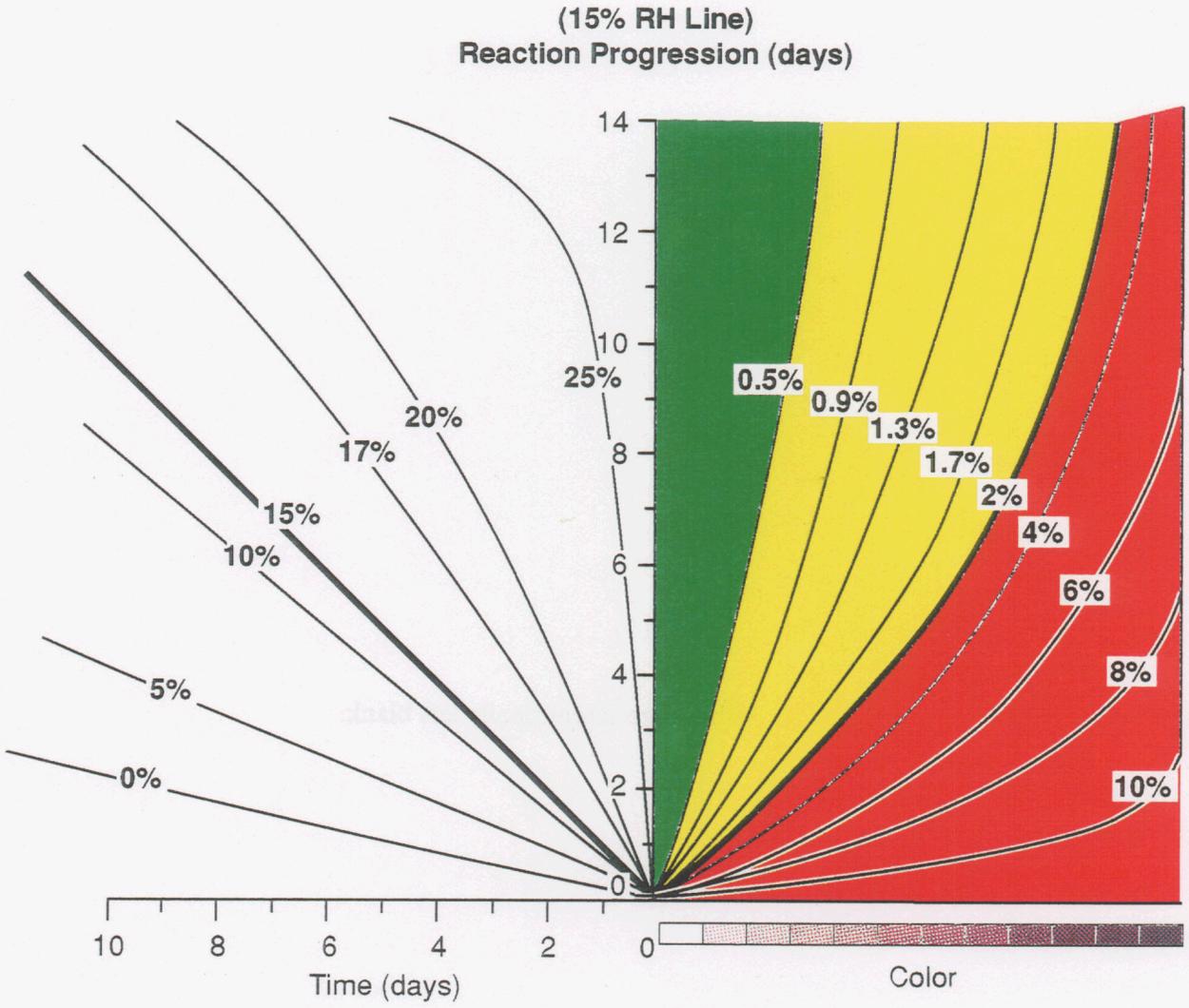


Fig. 8. Nitroester strip schematic calibration chart.

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5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

General results from this work are:

- Protocols for strip preparation, application, and monitor have been developed and improved.
- The strip indicator has been characterized at its present state of development.
- Strip indicator calibration has begun.

Specific developments during this phase of work are:

- AB and C reagents are best kept separate until time of indicator strip application. This helps avoid reactions amongst the reagents, which degrade the treated punches.
- Solutions give a more homogenous and easily monitored color than suspensions, due to the more even deposition of reagents on punches.
- Aqueous solutions are preferred over methanol-based solutions because they are cheaper, simpler and safer, and hold more solute.
- Tested Whatman cellulose filter backings are preferred primarily because they are thin yet flexible. The move away from glass fiber backings has, however, changed indicator tints from shades of red to purple.
- Dipping produces a more even distribution of reagents than spotting or rubbing. Further, predipped punches add to efficiency by making manual preparation easier and by allowing for simpler process automation.

5.2 RECOMMENDATIONS

Future tasks, not fully addressed in this funding cycle, include:

- Check for effect of AB "waxing" by multiple dipping, and known AB pipetting.
- Quantification by lux meter of light level effect. Detailed estimates of gross visible light level on reaction progression will be made to support the decision not to cover samples.

- Determination of casing humidity (%RH) effect on reaction by development of a humidity-controlled glove box for in-vitro sample preparation.
- Complete indicator calibration.
- Simulation by Intusoft ICAP/2 of lumped parameter diffusion models for scaling of in-vitro(petri) to in-vivo(casing) calibrations.
- Test of samples on recently nitroester-assayed casing sections to move check calibration scaling.
- Test for AB and C punch aging. Possible preventatives include: an inert gas environment, use of a desiccant, or an opaque light-excluding container.
- Test of indicator strips for flash combustibility at flame-front temperatures and times representative of chambered M829 (CCC) ignition.
- Environmental tests for indicator strip durability and legibility under field conditions (e.g., snow, rain, mud, dust, high/low light).

It is recommended that industrial collaboration now be obtained in the final development of the indicator and its evaluation in field trials.

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APPENDIX CALIBRATION AND CHARACTERIZATION BACKGROUND

Figures 10A and 10B show stills of videotape NG calibration data taken with predipped cellulose punches at 40%RH. Direct or video data provided sharpest color resolution, which was compared to the chart in Fig. 7 at a number of reaction times. The 6 photos of video shown in Figs. 10A and 10B were taken at 1.4, 4.3, 10.4, 19.9, 80.4, and 190.4 hours from the start of the indicator reaction. Five samples were set at each of 16 concentrations over a range of 0.1% to 8.0% (weight/weight):

Ctl	0.0%	D	0.4%	H	1.7%	K	5.0%
A	0.1%	E	0.5%	I	2.0%	L	6.0%
B	0.2%	F	0.9%	O	3.0%	M	7.0%
C	0.3%	G	1.3%	J	4.0%	N	8.0%

The unsmoothed results of these tests are shown in Fig. 11, which agrees well with expectations shown in Fig. 8. Though we had hoped for a range of 0.1% to 8.0%, upon review of Figs. 10A and 10B, we feel a stated range of only 0.5% to 8.0% is supportable at present. This is due to the rather weak response noted at 0.1% to 0.4%NG which is barely above that of the control (0.0%NG).

Figure 11 is used for the speed estimations cited in Sect. 4.2. Using the presumed model of Sect. 4 (i.e., exponential rise to a constant asymptote), *speed of reaction* is measured by time constant. The time constant determined from Fig. 11 is roughly 27, 18, and 11 hours, respectively, at 0.5%, 2.0%, and 8.0%NG; we report the mean average of 18.7 hours. However, in another sense, speed is best defined as best monitor time or *speed of monitor*. This is determined by finding the reaction time of widest color spread. This was found to be 37% cyan, occurring at 42 hours. A viewing window of 36 hours to 48 hours (1.5 days to 2.0 days) seems optimal, giving at worst a 33% cyan color spread. Resolution is then 33% cyan across the specified range and viewing window.

We defined accuracy as variance for a sample size of 5 taken at various concentration steps across the concentration range. Figure 12 shows standard deviation (normalized, 1 standard deviation = 6.3% cyan) vs time for various concentrations. Note that generally, accuracy improves with time and with concentration. At 95% confidence, the measured value of concentration is within $\pm 1.5\%$ of the true concentration.

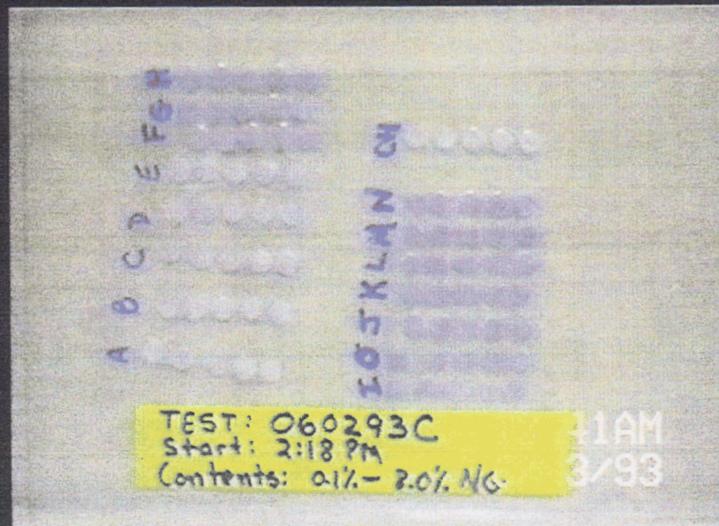
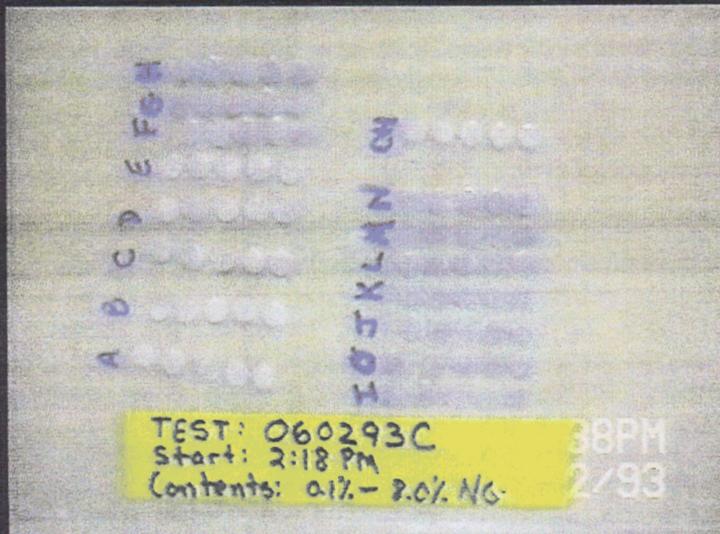
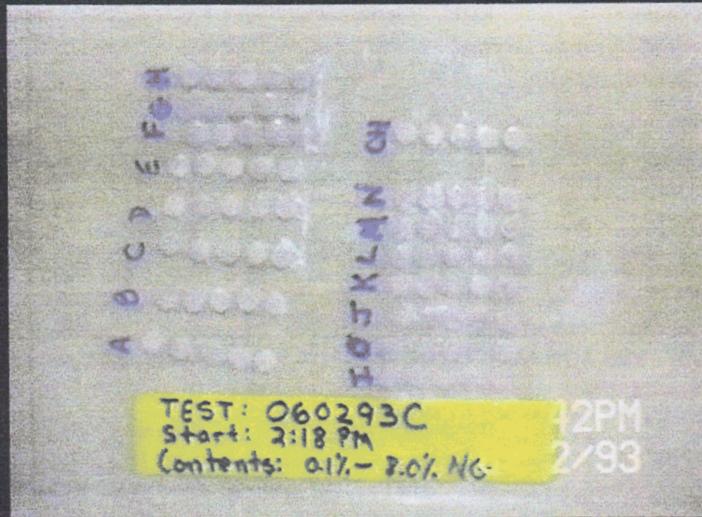


Fig. 10A. NG Color Progression After 1.4, 4.3, and 10.4 Hours (40%RH, Predipped Punches).



Fig. 10B. NG Color Progression After 19.9, 80.4 and 190.4 Hours (40%RH, Predipped Punches).

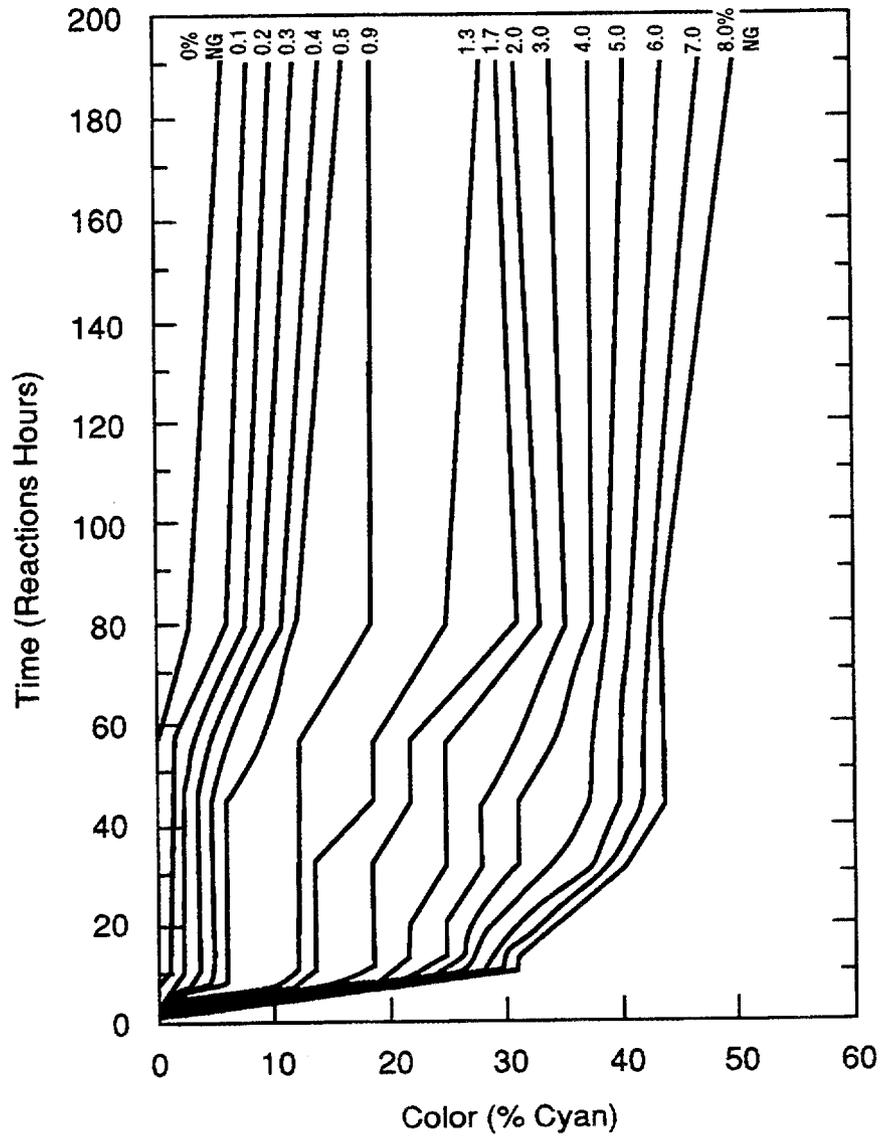
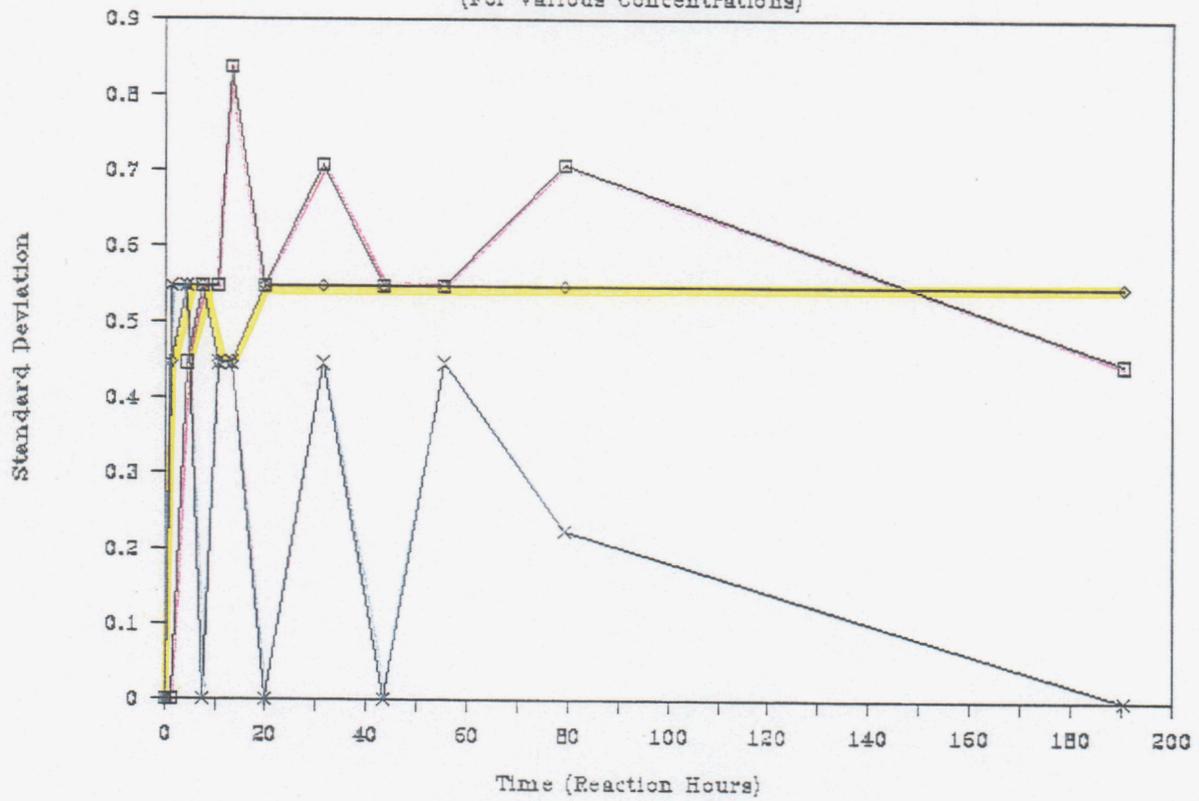
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Fig. 11. 40% RH Calibration (NG).

Fig. 12 Standard Deviation vs Time
(For Various Concentrations)



Key

Blue	8%NG
Yellow	2%NG
Red	0.5%NG

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