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COLORIMETRIC PERSONAL DOSIMETER FOR HYDRAZINE FUELS

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MINE SAFETY APPLIANCES COMPANY

MAY 1967

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COLORIMETRIC PERSONAL DOSIMETER FOR HYDRAZINE FUELS

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Foreword

The work reported herein was conducted by Mine Safety Appliances Company, 201 North Braddock Avenue, Pittsburgh, Pennsylvania 15208 under Contract No. AF 33(615)-2929, MSA Job No. AC-831. Solomon F. Brokeshoulder, Chemical Hazards Branch, Toxic Hazards Division, Biomedical Laboratory of the Aerospace Medical Research Laboratories, was technical contract monitor. The work was performed in support of project 6302, "Toxic Hazards of Propellants and Materials," Task 630203, "Identification of Toxic Materials." Charles A. Plantz was the principal investigator for Mine Safety Appliances Company assisted by Cecelia Jenca and Paul W. McConnaughey. The research was initiated in June 1965 and completed in August 1966.

This technical report has been reviewed and is approved.

WAYNE H. McCANDLESS
Technical Director
Biomedical Laboratory
Aerospace Medical Research Laboratories

Abstract

A research program was initiated to develop a personal colorimetric dosimeter for hydrazine fuels. An extensive literature survey was conducted to ascertain the most appropriate colorimetric reactions applicable to such a device. Many reagents were found which formed a color upon contact with various hydrazine vapors; however, most of these colored reaction products proved unstable during accelerated aging tests. Bindone, ($\Delta^{1,2'}$—Biindan)—1′,3,3′—Trione, uniformly dispersed on Eastman Chromagram Sheet (Type K301R2) was selected for incorporation as the sensing element in the dosimeter badge, because its response to hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH) was both linear and readily observable. Synthetic color standards were developed and included in the dosimeter to provide the user with a means of estimating accumulated exposure within the range of 100-1800 ppm-minutes.

SECTION I.

Introduction

Fuel handlers and other personnel in the immediate vicinity of propellant operations may be inadvertently exposed to toxic concentrations of airborne vapors of the different hydrazine fuels, hydrazine, monomethylhydrazine (MMH), or unsymmetrical dimethylhydrazine (UDMH).

A device is required to alert these personnel to a potentially hazardous environment and also to provide medical personnel with estimates of individual exposures. The operational requirements of such a device demand that it contain no moving parts, be light in weight, require no external source of power, be simple to operate, and be compatible with field operations. To this end, a research program was initiated to develop a colorimetric personal dosimeter.

The approach to the development of this colorimetric dosimeter was guided by three considerations: (1) the color formed by contact with vapors of the hydrazine fuels must be distinct, reproducible, and long-lasting; (2) the color must darken continually on prolonged contact with the airborne fuel vapor; and (3) the color must indicate the approximate integrated exposure by visual comparison with three synthesized color standards that correspond to Emergency Exposure Levels (EEL) or Threshold Limit Values (TLV) for the fuels hydrazine, MMH, or UDMH.

An extensive literature survey showed that most analytical procedures for hydrazine and its derivatives consisted of oxidation-reduction (ref 4), acid-base (ref 7) titrations, or gasometric (ref 6) methods.

The common analytical methods, such as infrared, chromatography (gas and paper), fluorometry, turbidimetry, amperometry, refractometry, and gravimetry have been adapted to hydrazine analysis. The MSA Billion-Aire, a continuous recording instrument based on suppression by contaminants of an alpha particle induced ion current, has been calibrated for ppm concentrations of UDMH and MMH in air. Forty-seven literature references were found describing colorimetric analyses and color tests for hydrazines. Most of the literature methods had never been used for low concentrations of hydrazines in air.

Some of the colorimetric reagents may be grouped together because of similarity of reaction. The most popular group includes p-dimethylaminobenzaldehyde, salicylaldehyde, and vanillin (ref 10) and 2-hydroxy-1-naphthaldehyde (ref 8). These compounds form colored or fluorescent azines with hydrazine. Another group consisting of copper, silver, and gold compounds (ref 3) gives a color due to the formation of finely divided metal or reduction to a lower valence state. Picryl chloride (ref 5) is a pi-acid due to its polynitro-substituted aromatic nucleus. It is the only pi-acid found in the literature as having been used for analysis of hydrazines. Many other pi-acids, however, such as trinitrobenzene, trinitrofluorenone, tetranitrofluorenone, and 9-dicyanomethylene-2,4,7-trinitrofluorene are known to give colors with pi-bases, and were therefore tested.

Many other compounds not easily classified were found in the literature. These include selenium dioxide (ref 2), chromic acid, complex molybdates, 2-nitro-1, 3-indanedione (ref 11), calcium chloride-potassium cyanate-dimethylglyoxime, and various dyes, such as rhodamine B, gallein, and aurin. Bindone, ($\Delta^{1,2'}$–Biindan)–1′,3,3′–Trione,* the compound finally chosen, has been studied extensively by the Institute of Organic Synthesis of the Latvian Academy of Sciences, Latvia, USSR. Investigators of the Institute have developed a colorimetric method of analysis for hydrazine using bindone in acetic acid (ref 12) as the reagent.

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*Product of the Aldrich Chemical Co.

SECTION II.

Selection of Reagents

Sixty-three reagents in 195 different formulations were tested. The most applicable of these formulations are found in appendices I, II, and III with results of sensitivity and stability tests.

Reagents were tested on silica gel in tubes and dispersed on transparent tape. In other tests, the reagents were impregnated in five kinds of cellulose paper, fiberglass paper, Eastman Chromagram Sheet (ECS)*, and coatings of silica gel and polyvinyl alcohol on glass plates. Impregnated gels dispersed on tape are more sensitive than gels in glass tubes, presumably because of the barrier to diffusion presented by the fiberglass plug in the end of the tube open to the air. ECS, a polyester film coated with a layer of silica gel 100 μ thick, is often more sensitive than paper because of the uniformly thin layer and catalytic effect of silica gel. Silica gel coatings on glass plates were also tried without marked success. The gel was deposited on the plates by first drying a sodium silicate solution on the plate and then treating it with dilute acid.

Most of the reagents of the aldehyde type were not sensitive enough and the original color from p-dimethylaminobenzaldehyde faded on prolonged contact with higher concentrations of hydrazines vapors. Reagents of the pi-acid or polynitro aromatic type were more sensitive. 2,4,5,7-tetranitrofluorene-9-one (TENF) was one of the most sensitive of all the reagents found during the study. Picryl chloride, trinitrobenzaldehyde, and 9-dicyanomethylene-2,4,7-trinitrofluorene were also sensitive.

Selenium dioxide was sensitive but developed a strong foul odor on exposure to hydrazines. Trisodium pentacyanoammineferrate-(II), gold and silver salts, and bindone, in general, were very sensitive. However, bindone appeared to exhibit a relative sensitivity in that its response to UDMH and MMH was more intense than to hydrazine. Sodium molybdate in sulfuric acid was dispersed on silica gel on glass plates because it turned blue on contact with untreated Eastman Chromagram Sheets. The molybdate salt was very sensitive but was difficult to dry without discoloration.

Several insoluble silver salts were synthesized in an attempt to eliminate the phototropic sensitivity of soluble silver salts. However, the ractivity of silver stearate, which was the most applicable salt, depended on the way in which it was precipitated. Silver stearate precipitated on paper showed good relative sensitivity but its stability was marginal. A large number of different insoluble silver salts were synthesized and tested for improved stability. These are listed in appendices II and III. In general, the more soluble the silver salt, the more sensitive it was but less stable. Since the stearate was the most promising silver reagent, several different methods of preparation were tried. Apparently minor variations in the method of precipitating the silver stearate gave major variations in its sensitivity and chemical stability. The usual way to prepare silver stearate paper is to dip the paper in sodium stearate solution, then into silver nitrate solution. In addition, if the reagents were applied in the reverse order, the sensitivity was drastically reduced. If the sodium stearate solution was allowed to age, the sensitivity was also reduced. The greatest improvements in stability and relative sensitivity were obtained by using humectants and by substituting tetramethyl ammonium stearate for sodium stearate. Unfortunately, every increase in sensitivity was accompanied by a corresponding decrease in chemical stability. The disadvantages of the silver salts outweighed the advantages; therefore, they were not further considered.

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*Product of Eastman Kodak Co., Rochester, New York.

Stability tests were performed by sealing the sensitized papers or film in a glass tube under a nitrogen atmosphere. Some were sealed in plastic packs with air in the sealed space. The samples were then aged at 65 C for 7 days. Our own experience showed that 65 C for one week is approximately equivalent to aging for one year at room temperature. Only bindone, of all the highly sensitive reagents, was stable on accelerated aging. However, bindone had to be purified before it could be used.

Upon consideration of all the characteristics of the reagents tested, such as sensitivity, stability, and ease of preparation, TENF was selected initially as the sensing material for the dosimeter. However, completion of a few additional experiments with bindone revealed that certain improper procedures resulted in erroneous conclusions concerning the sensitivity of this reagent. In earlier studies, various vapor concentrations of hydrazine were used to calibrate the sensors under static conditions. Investigations revealed that during these static tests the hydrazine was strongly adsorbed on the walls of the test containers resulting in a significant loss in vapor concentration. Subsequent calibration of the sensors under dynamic conditions obviated the objection to the relative sensitivity of bindone. In addition, we found a solution of bindone in dioxane was stabilized on ECS by the prior addition of a dilute solution of oxalic acid. Therefore, bindone was selected as the most suitable reagent for the dosimeter.

SECTION III.

Badge Preparation and Testing

Four engineering prototype badges were fabricated and tested. Refinements in the design were made after each test. Each badge was tested for uniformity and reproducibility of exposure of the sensor to vapors of the hydrazine fuels and protection of the sensor from direct light. A diagram of the final design is shown in figure 1. The basic badge is made from vacuum formed plastic as shown in figures 2 and 3. The external dimensions are 3.3 by 5.2 by 1.2 cm with a 0.2 by 1.4 cm trough to hold the sensor strip. Since the sensitivity of the strip is reduced by exposure to direct light, it was necessary to incorporate a protective shield. A No. 8 Wratten filter furnishes protection for the strip and simultaneously permits the wearer to observe the discolored segment of the sensor strip and compare it with the synthesized color standards to estimate the integrated exposure.

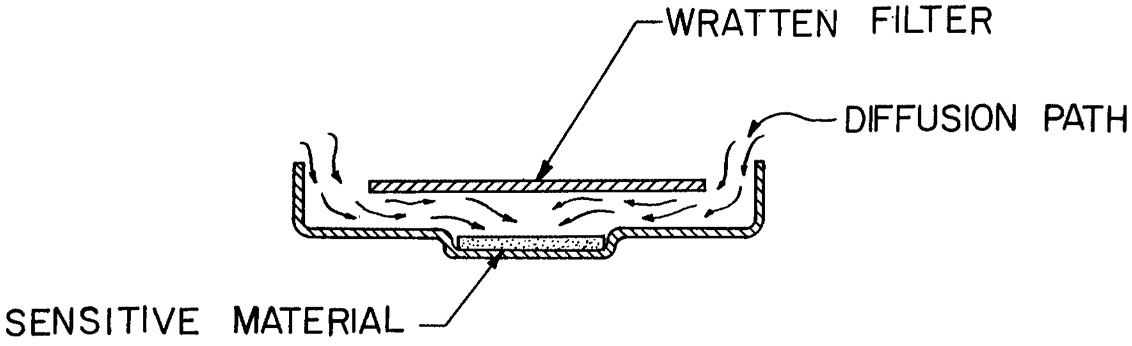

Figure 1. Diagrammatic View of Dosimeter

Dyes for use in preparing color standards were tested for stability in sunlight because the color standards will be only partly protected by the light shield of the badge. These permanent color standards were prepared to match the hue, chroma, and intensity of the color formed by the reaction of bindone and vapors of the hydrazine fuels. The No. 8 Wratten filter and the color standards exhibited no change in color when tested against saturated UDMH vapors for about 15 minutes.

PREPARATION OF BINDONE ON EASTMAN CHROMAGRAM SHEET

Bindone is purified by solid-liquid chromatography using a silica gel column, eluting with a 1:3 dioxane-benzene mixture, and then crystallizing from the evaporated eluate. The ECS (in 8-inch squares) is washed 10 times with dioxane and treated with a large excess (10 ml) of 0.5% oxalic acid monohydrate in dioxane. The excess is drained by setting the ECS on edge on paper towels in a chamber saturated with dioxane vapors for 15 minutes. The treated square is dried at 65 C. Five ml of a 1% solution of purified bindone in dioxane is added and the excess drained and dried as before. The chamber filled with dioxane vapors is necessary to insure uniform impregnation of the large pieces; the saturated atmosphere prevents any evaporation while the solutions are traversing the 8-inch distance.

The edges of the 8-inch squares are trimmed 3-4 mm, and the material is cut into 14 by 41 mm rectangles. Six of these are heat-sealed in paper-aluminum foil-plastic envelopes, and one envelope is included in each kit.

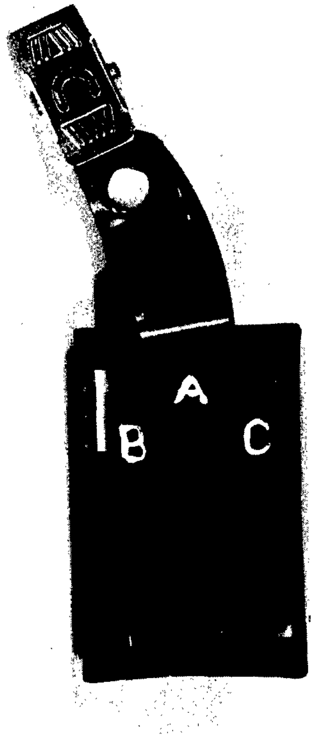

Figure 2. Front View of Dosimeter with Light Shield in Place

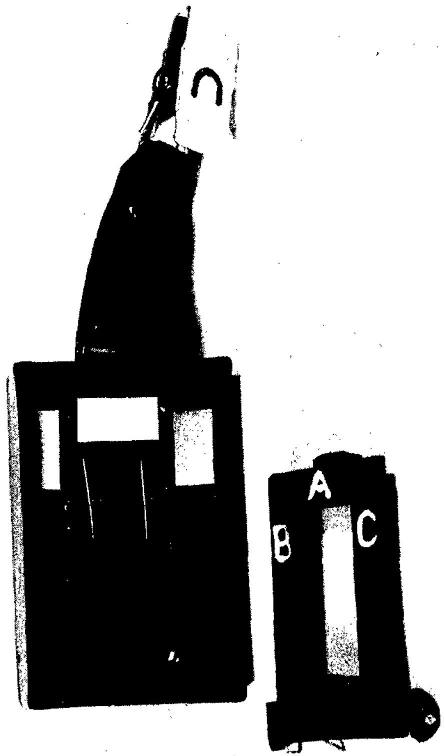

Figure 3. Front View of Dosimeter with Light Shield Removed

TEST METHODS

Gas mixtures for final calibration were prepared in an all-glass double dilution apparatus; nitrogen was bubbled through hydrazine fuels into the apparatus where the saturated stream was diluted with air purified by an MSA all-service canister. The effluent from the mixer was passed into a 4-liter bottle containing the badges to be calibrated, and the effluent vapors were analyzed during the development of color.

Analysis of concentrations of UDMH and MMH was performed by absorbing about 100 liters in glacial acetic acid in a bubbler, and titrating with 0.1 N perchloric acid in glacial acetic acid using methyl violet indicator. N_2H_4 analyses were performed by absorbing 1.5 liters of effluent in 1% aqueous hydrochloric acid, followed by the ASTM colorimetric method using p-dimethylaminobenzaldehyde (ref 1). Two bubblers in series were used for all three analyses with no hydrazine being absorbed in the second bubbler. The concentrations in the effluent could also be calculated from the known vapor pressures of the three hydrazines and the ratio of flow in the two stages of dilution. Calculated and analyzed values agreed for UDMH, but the analyzed values for MMH and N_2H_4 were slightly lower. The analyzed values were used for calibration.

CALIBRATION

Color standards were prepared for approximately 65, 270, and 1200-ppm-minutes of UDMH. These standards were then calibrated for MMH and hydrazine exposures. The standards are designated A, B, and C in order of increasing depth of color. The final calibration values are tabulated in table I.

TABLE I.

COLOR STANDARD VALUES

Fuel Used	*Color Standard Matched*	*Concentration-Time Value of Hydrazine (ppm minutes)*
UDMH	A	65
UDMH	B	270
UDMH	C	1200
MMH	A	100
MMH	B	400
MMH	C	1100
N_2H_4	A	200
N_2H_4	B	700
N_2H_4	C	1800

The calibration was performed at 25 C, 30% R.H., and 10 ppm. Variations in temperature from 5 to 50 C and humidity from 0 to 100% caused negligible changes in calibration. Variations in the concentration of bindone also caused changes in calibration.

SECTION IV.

Summary

A useful colorimetric personal dosimeter to detect vapors of hydrazine, MMH, and UDMH has been developed. Its operation is based on the purple color formed with bindone dispersed on ECS. The sensitized film is affected by light, but the dosimeter badge incorporates a yellow filter to protect the film from direct light. The badge is not intended for use as an analytical device but rather as a means of warning the user of a hazardous environment. In addition, it can provide medical personnel with an estimate of the integrated exposure (ppm-minutes). The color developed for hydrazine is greyer than that for MMH or UDMH and, accordingly, does not match the color standards as well. Once developed, the color changes only slightly during a period of 12 hours, which is commensurate with the operational requirements.

SECTION V.

Recommendations for Future Developments

1. A spray or dip might be developed to coat the exposed sensitive film rendering the color permanent.

2. Attempts were made during this contract to synthesize two different nitrosubstituted bindones. More work along this line could be done to synthesize bindones substituted with alkyl, alkoxyl, nitro- or halo-groups starting with the corresponding phthalic acids.

3. Other thin layer chromatography materials might be substituted for Eastman Chromagram Sheet.

4. The No. 8 Wratten filter should be held in a frame which allows for slight expansion or contraction.

5. Different color standards are needed if the badge is to be used extensively for N_2H_4.

6. 4-bromo- or 4-iodo-2,5-7-trinitrofluorenone, a powerful new pi-acid should be investigated as an alternative reagent (ref 9).

APPENDIX I.

FORMULATIONS OF REAGENTS

Lot No.	*Formulation*	*Sensitivity**	*Stability***
1	Salicylaldehyde on silica gel	CV	–
3	p-dimethylaminobenzaldehyde on silica gel	L	–
35	p-dimethylaminobenzaldehyde on paper	L	–
15	Same as (3), but 5 x conc. of DAB	L lot 3	–
16	Same as (15), but HCl added	L lot 15	–
5	Vanillin on silica gel	L	–
21	2-hydroxy-1-naphthaldehyde on silica gel	CV	–
19	2,4-dihydroxyacetophenone	I	–
25	Picryl chloride on silica gel	M	–
31	Picryl chloride on paper	M-H	$U(N_2)$
31a	Picryl chloride on Eastman Chromagram sheet (ECS)	M-H	$U(N_2)$
36	Trinitrobenzene on paper	I	–
39	2,4,6-Trinitrobenzaldehyde on ECS	H	$U(N_2)$
41	Trinitrobenzoyl chloride on ECS	M-H	–
40	3,5-dinitrobenzoyl chloride on ECS	I	$U(N_2)$
38	9-dicyanomethylene-2,4,7-trinitrofluorene on ECS	H	$U(N_2)$
52	Picryl acetate on ECS or paper	H	–
53	3-nitrophthalic anhydride on ECS or paper	I	–
30	2,4,7-trinitrofluorene-9-one on ECS	M	$U(N_2)$
32	2,4,5,7-tetranitrofluorenone on ECS	H	$U(N_2)$
155-7	Same as 32, but with 3 humectants added	H lot 32	–
53	3-nitrophthalic anhydride on ECS or paper	I	–
27	2-nitro-1,3-indanedione on gel	I	–
7	$CaCl_2$ + KCNO + dimethylglyoxime + HCl on gel	I	–
10	Selenium dioxide on gel	M	–
34	Selenium dioxide on paper	H	–
P5, P6	Selenium dioxide on silica gel on glass plate	H	–
17	$CUSO_4$ + tetramethyldiaminodiphenylmethane + salicylic acid + silica gel	M	–
33	Trisodium pentacyanoammineferrate-(II) on ECS	H	$U(N_2)$
54	Rhodamine B on ECS	I	–
55	Gallein on ECS	I	–
56	Aurin on ECS	M	–
87	Methyl violet on polystyrene beads	CV	–
43	Copper sulfate on paper	M	–
46	Gold chloride + glycerine on ECS	H	–
44	Silver nitrate + glycerine on ECS	H	–
47	Silver sulfate + glycerine on ECS	H	$U(N_2)$
48	Silver perchlorate + glycerine on ECS	H	$U(N_2)$
83	Silver fluoride + glycerine on ECS	H	$U(N_2)$
49	Silver cyanide + potassium cyanide + glycerine on ECS	I	–
76	Silver chloride + sodium thiosulfate on ECS	I	–
P2	Chromic acid + sulfuric acid on silica gel on glass plate	M	–
P3, P4	Sodium molybdate + sulfuric acid on silica gel on glass plate	H	–
18	Bindone on silica gel	M	–
29	Bindone + acetic acid on silica gel	M≅lot 18	–
37	Bindone on paper	H	$S(N_2)$
37a	Bindone on Eastman Chromagram sheet (ECS)	H>lot 37	$U,S(N_2)$
147	Bindone + glycerine on ECS	H ≅ 37a	$S(N_2)$
148	Bindone on ECS (0.520 x concentration of lot 37a)	H ≅ 37a	$S(N_2)$
149	Bindone + emulphogene BC-840 on ECS	H ≅ 37a	$S(N_2)$
150	Bindone + sorbitol on ECS	H ≅ 37a	$S(N_2)$
163	Bindone + tetranitrofluorenone on ECS	H ≅ 37a	
165	Bindone on ECS previously treated with 1% oxalic acid in dioxane	H ≅ 37a	–
166	Same as lot 165, but 0.1% oxalic acid	turned spontaneously	
167	Same as lot 165, but 0.5% oxalic acid	H ≅ 165	$S(N_2)$

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*In the sensitivity column: I indicates insensitive; CV indicates sensitive to concentrated vapors only; L indicates C-T values of 10,000 ppm-minutes or more to moderate color; M indicates C-T of 1000-10,000 to moderate color; H indicates C-T values of 100-1000 to moderate color.

**In the stability column: S indicates no change in 1 week at 65 C; U indicates unsatisfactory; (N_2) indicates aging test done sealed in nitrogen.

– indicates test was not performed.

APPENDIX II.

INSOLUBLE SILVER SALTS ON PAPER

Lot No.	*Soluble Salt Used to Precipitate Silver Salt on Paper*	*Sensitivity*	*Stability*
60	NaOH + stearic acid	H	$S(N_2)$
57	Potassium ferricyanide	M	—
58	Sodium carbonate	H	$U(N_2)$
59	Sodium chloride	M	$U(N_2)$
61	Trisodium phosphate (Na_3PO_4)	H	$U(N_2)$
62	Sodium silicate	Turned black spontaneously	
63	Sodium pyrophosphate ($Na_4P_2O_7$)	H	$U(N_2)$
64	Sodium caproate	H	$U(N_2)$
65	Sodium tetraborate	H	$U(N_2)$
66	Potassium acid phthalate	M	$U(N_2)$
67	Potassium oxalate	M	$U(N_2)$
68	Potassium thiocyanate	H	$U(N_2)$
69	Sodium metaphosphate ($NaPO_3$)	M	—
70	Sodium tungstate	H	$U(N_2)$
71	Sodium aluminate	H	$U(N_2)$
72	Sodium citrate	H	$U(N_2)$
74	Sodium phosphate (secondary) (Na_2HPO_4)	H	$U(N_2)$
75	Sodium molybdate	L	—
136-140	Potassium thiocyanate (5 different humectants) put on paper just before drying)	H little or no improvement over lot 68	$U(N_2)$
145	Sodium abietate	I	—

Whatman No. 3 paper was dipped in a solution of the soluble salt and then in silver nitrate solution, then washed several times in deionized water, and dried.

APPENDIX III.

VARIATIONS ON SILVER STEARATE

Lot No.	*Way In Which Each Lot Differs From Lot 60*	*Sensitivity*	*Stability*
79	Sodium oleate instead of sodium stearate	H>lot 60	$U(N_2)$
80	Sodium palmitate instead of sodium stearate	H≅lot 60	$U(N_2)$
81	Sodium nonadecanoate instead of sodium stearate	M<lot 60	$S(N_2)$
82	Sodium stearate dissolved in methanol instead of water	M	—
84	Silver perchlorate instead of silver nitrate	H	—
85	Same as 84, but reverse reaction, that is,	L	—
	paper dipped in $AgClO_4$ first then in sodium stearate	H<lot 60	—
86	Reverse reaction	M	$U(N_2)$
88	Potassium stearate instead of sodium stearate	M	$S(N_2)$
89	Same as 88, but reverse reaction	L	$U(N_2)$
90 & 93	Bought sodium stearate, instead of its being made from sodium hydroxide solution and excess stearic acid	H-M	$S(N_2)$
91	Same as 90, but reverse reaction	H<lot 90	$U(N_2)$
92	Sodium heptadecanoate instead of sodium stearate	M	$U(N_2)$
94	Same as 91, but $AgNO_3$ saturated paper plastered on cold gelled sodium stearate solution, so silver stearate forms on one side only	H<lot 60	$U(N_2)$
95	10% $AgNO_3$ solution instead of 1%	H<lot 60	$S(N_2)$
96	Same as 95, but reverse reaction	I	$U(N_2)$
97	0.25% $AgNO_3$ solution instead of 1%	I	—
98	Paper dipped in sodium stearate, then in $AgNO_3$ then back in sodium stearate	I	—
99	Same as 98, but glycerine added	I	—
100	Same as 95, but glycerine added	H>lot 60	—
101	Silver citrate precipitated on paper, then attempted to replace citrate ion by stearate ion, by long soaking in sodium stearate	I	$U(N_2)$
102	Same as 101, but silver pyrophosphate instead of silver citrate	I	$U(N_2)$
103 & 104	Silver hydroxide precipitated on paper, then soaked in stearic acid in isopropyl alcohol	L	—
105	Glycerin added	H≅lot 60	$U(N_2)$
106	Sorbitol added	H>lot 60	$U(N_2)$
107	2,2′-Thiodiethanol added	L	—
108	Diethylene glycol added	M	$U(N_2)$
109	Triethanolamine added	H>lot 110	$U(N_2)$
110	Carbowax 1540 added	H>lot 106	$U(N_2)$
111	10% silver nitrate instead of 1% and sorbitol added	M	$U(N_2)$
112	Same as 111, but glycerin instead of sorbitol	H≅lot 105	—
113	Same as 111, but mannitol instead of sorbitol	M≅lot 111	—
114 & 115	Same as 111, but polyvinylpyrrolidinone instead of sorbitol	M≅lot 111	$U(N_2)$
116	Same as 111, but Alipal EO-526* added instead of sorbitol	H>lot 111	$U(N_2)$
117	Same as 111, but Igepal CO-630* added instead of sorbitol	H≅lot 111	$U(N_2)$
118	Same as 111, but Emulphogene BC-840* added instead of sorbitol	H≅lot 111	$U(N_2)$
119	Same as 111, but Alkanol HCS* added instead of sorbitol	H≅lot 111	$U(N_2)$
120	Sodium stearate solution 3 times as concentrated	M	$U(N_2)$
121	Sodium docosanoate instead of sodium stearate and 10% silver nitrate	H<lot 60	$U(N_2)$
122	Same as 121, but glycerin added	H<lot 121	—
123	Same as 121, but Emulphogene BC-840 added	H<lot 121	$U(N_2)$
124	Same as 121, but Alipal CO-630 added	H<lot 121	$U(N_2)$
129	Stoichiometric sodium stearate instead of excess stearic acid, and 10% silver nitrate	H<lot 60	$U(N_2)$
126	Same as 129, but glycerin added	H>lot 129	—
127	Same as 129, but Emulphogene BC-840 added	H>lot 129	$U(N_2)$
130	Same as 129, but Emulphogene BC-840 added to sodium stearate solution before reaction	H>lot 60	$U(N_2)$
131	Same as 129, but tetraethyl ammonium stearate instead of sodium stearate	H<lot 60	$U(N_2)$
132	Same as 131, but Emulphogene BC-840 added	H≅lot 131	$U(N_2)$
133	Same as 132, but reverse reaction	L	
134	Same as 131, but Emulphogene BC-840 added to tetraethyl ammonium stearate before reaction	H>lot 131	$U(N_2)$
135	Same as 134, but reverse reaction	M	
141	Same as 131, but tetramethylammonium stearate instead of tetraethylammonium stearate	H>lot 131	$U(N_2)$
142	Same as 141, but Emulphogene BC-840 added	H>lot 141	$U(N_2)$
143	Same as 141, but ECS instead of paper	H≅lot 141	
144	Same as 141, but 10% $AgClO_4$ instead of $AgNO_3$	H≅lot 141	$U(N_2)$

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*A polyoxyethylene surfactant

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13. ABSTRACT

A research program was initiated to develop a personal colorimetric dosimeter for hydrazine fuels. An extensive literature survey was conducted to ascertain the most appropriate colorimetric reactions applicable to such a device. Many reagents were found which formed a color upon contact with various hydrazine vapors; however, most of these colored reaction products proved unstable during accelerated aging tests. Bindone, ($\Delta^{1,2'}$—Biindan)—1′,3,3′—Trione, uniformly dispersed on Eastman Chromagram Sheet (Type K301R2) was selected for incorporation as the sensing element in the dosimeter badge, because its response to hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH) was both linear and readily observable. Synthetic color standards were developed and included in the dosimeter to provide the user with a means of estimating accumulated exposure within the range of 100-1800 ppm-minutes.

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