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AEROSOL EXPLOSIVE INDICATOR KIT

F. T. Sweeney, et al

Franklin Institute Research Laboratories  
Philadelphia, Pennsylvania

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## FOREWORD

This report is submitted in compliance with contractual requirements as directed by the U.S. Army Land Warfare Laboratory, Aberdeen Proving Ground, Maryland, under Contract No. DAAD05-74-C-0723. Mr. J. L. Baer, Chief Applied Chemistry Branch, served as Technical Supervisor for the work, and we would like to acknowledge his insights and assistance during the project.

Principal Investigators for the program at The Franklin Institute Research Laboratories were Mr. F. J. Sweeney, Research Chemist and Dr. P. W. D. Mitchell, Principal Scientist. Other FIRL personnel contributing significantly to the program were Dr. R. Florentine and Mr. E. Evans of the Physical and Life Sciences Department.

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## 1. INTRODUCTION

Many explosive devices are currently being fabricated and used in indigenous devices against civilian and military personnel both in this country and abroad. Currently there are no known simple and economical devices that can give a quick, positive identification of the presence of traces of explosive residues that may be found on the outside of a container or on the hands and clothing of the individual who has packaged the explosive.

Having determined the feasibility of an aerosol spray detector in a previous study (Contract DAAD05-73-C-0140) in which 5% aqueous ethylenediamine was used to detect traces of polynitro aromatic explosives on paper and human skin, it was attempted in this work assignment to increase, if possible, the sensitivity of this reagent while reducing its toxicity. It was also required to investigate the common chemical indicators and dyes suitable for detection of trace quantities of explosives and to adapt or modify them so they could be incorporated into an aerosol spray device. These reagents should give a detectable color change when coming into contact with traces of explosives on packages, clothing and human skin while being simple enough to be used by untrained personnel.

A specific requirement of this task was to attempt to eliminate strong acids or bases normally required to produce the colors indicated by an explosive in laboratory tests and to attempt to use instead UV or IR radiation as the activating agent.

The explosives tested were: Dynamite, trinitrotoluene, pentaerythritol tetranitrate (PETN) and C-3. These were chosen for several reasons; most importantly they are the ones most commonly used in letter bombs. Secondly, they represent several chemical classes of high explosives.

For example, trinitrotoluene is classified as an aromatic nitro compound; dynamite and pentaerythritol-tetranitrate as aliphatic nitrate ester; C-3 is a plastic composite explosive consisting mainly of Cyclonite, a cyclic aliphatic compound. The structure of these explosives is shown in Figure 1.

It is also desirable that the chosen indicator systems possess the following properties:

1. The reagents must not destroy the suspected container's integrity.
2. They must not be hazardous to personnel.
3. They must not give false positives. More importantly, they must not give false negatives.
4. They must be stable for three months or more.
5. It is desirable, but not essential, that they be specific for a particular explosive.

	1% Diphenyl Amine in Ethanol + UV in 5-10 sec.	2% Starch + 2% KI + DMSO - 20% + 3 min. Heat + H <sub>2</sub> O	Aqueous Sol'n-80%	5% Ethylene- Diamine in CHCl <sub>3</sub> (from previous study)
$\begin{array}{c} \text{NO}_2 \\   \\ \text{O} \\   \\ \text{CH}_2 \\   \\ \text{O}_2\text{NOCH}_2\text{C}-\text{CH}_2\text{ONO}_2 \\   \\ \text{CH}_2 \\   \\ \text{O} \\   \\ \text{NO}_2 \end{array}$ <p>Aliphatic Nitrate Ester</p> <p>PETN (Pentaerythritoltetranitrate)</p>	Yellow green		Blue	NR
$\begin{array}{c} \text{NO}_2 \\   \\ \text{H}_2\text{C} \quad \text{N} \quad \text{CH}_2 \\   \quad \quad   \\ \text{O}_2\text{N}-\text{N} \quad \text{C} \quad \text{N}-\text{NO}_2 \\   \quad \quad   \\ \text{H}_2 \end{array}$ <p>Cyclic Aliphatic Compound</p> <p>77% Cyclonite = RDX</p>	NR	NR	NR	Wine Red
$\begin{array}{c} \text{CH}_3 \quad \text{NO}_2 \\   \quad \quad   \\ \text{O}_2\text{N} \quad \text{N} \quad \text{NO}_2 \\   \\ \text{NO}_2 \end{array}$ <p>3% Tetryl</p>				
$\begin{array}{c} \text{CH}_3 \\   \\ \text{O}_2\text{N} \quad \text{C}_6\text{H}_3 \quad \text{NO}_2 \\   \\ \text{NO}_2 \end{array}$ <p>Aromatic Nitro Compound</p> <p>TNT (2,4,6 Trinitro-toluene)</p>	NR		NR	Wine Red
$\begin{array}{c} \text{CH}_2\text{O}-\text{NO}_2 \\   \\ \text{CH} \text{O}-\text{NO}_2 \\   \\ \text{CH}_2\text{O}-\text{NO}_2 \end{array}$ <p>Aliphatic Nitrate Ester</p> <p>Glyceryl Trinitrate (Dynamite)</p>	Yellow green		Blue	NR

NR - No Reaction

Figure 1. Summary of Results of Explosives Tested



## 2. EXPERIMENTAL

During the first phase of this study, an extensive literature search was conducted. The search included technical literature on explosives, basic organic chemistry of nitro compounds, basic texts on qualitative organic analysis, and monographs on thin layer and paper chromatography with emphasis on visualization reagents. Requests were made to DDC for computer searches both classified and unclassified. The searches were conducted with emphasis on chemical detection of explosives. "Explosives and Munitions Detection Review QMDO" was obtained from DDC. Its contents were thoroughly evaluated with special emphasis on chemical detectors.

A computerized search was also carried out at FIRL's Science Information Services using Chemical Abstracts Condensates which contain all papers indexed by Chemical Abstracts from 1970 to the present, and a search was made by the National Technical Information Service which abstracts the unclassified government literature. FIRL also obtained directly from DDC a search which included classified reports. A broad base of key words was given to the computer so in addition to useful information there was quite a bit of "random noise."

Unfortunately in all the above searches, no work was found on detection of explosives at trace levels which use conditions and reagents mild enough for determination on skin and paper. Several sources such as texts and monographs were also consulted. These are listed in the bibliography.

A form letter was composed and sent to several manufacturers of explosives requesting information on detection of traces of explosives. Although replies were received from almost all companies contacted, none gave any information regarding analysis of trace quantities. This is surprising in view of the current trend toward analysis of chemicals at

the trace and sub-trace levels and the recent findings of heart problems in workers retired from explosive manufacturing plants.

Several off-the-shelf chemicals were tried while waiting for reagents and supplies. One of these was Kodak D-76 which gives a positive color test for a few explosives but is not sensitive or selective enough. Diethylaminoethanol is a reagent commonly used to detect explosives. This reagent gave no color reaction when sprayed on explosives as a neat liquid or 10% in ethanol. Another spray reagent tried was amino-G-acid (2-naphthalene-6, 8-disulfonic acid) 0.2% in ethanol followed by spraying with 1%  $\alpha$ -naphthyl amine in dilute HCl. In trial runs with new chemicals a solution of m-dinitro benzene in acetone was used for evaluation of reagents. Spots of the solution on filter paper were treated with various chemicals with the following results:

- a. Ethylene diamine  $\rightarrow$  strong red color
- b. EDTA (di sodium salt)  $\rightarrow$  no color
- c. Methyl hydroquinone (acetone solution)  $\rightarrow$  yellow color
- d. Above (c) plus ammonia  $\rightarrow$  deeper yellow color which lasts longer
- e. Polyethylene imine  $\rightarrow$  yellow
- f. Methyl hydroquinone plus pyridine  $\rightarrow$  yellow (lasts)
- g. Benzil in acetone  $\rightarrow$  no color
- h. Benzil plus KOH  $\rightarrow$  pale yellow

For determination of the sensitivity of methyl hydroquinone, a 0.5% solution of m dinitro benzene in acetone was made up. One drop (approximately 0.15 mg) spotted on paper was easily detected by methyl hydroquinone by the yellow color. The dinitro benzene solution was diluted 0.5 ml to 50 mls and a drop on paper again tested.

The spot (containing about 2  $\mu$ g) when treated with methyl hydroquinone gave a barely visible yellow color. This represents the lower limit of detectability by the methyl hydroquinone reagent.

The same amount of dinitro benzene treated with ethylene diamine gave an easily seen pink color.

Other hydroquinones such as hydroquinone and 2,3-dihydroxy naphthalene give yellow colors with dinitro benzene, but the test is not satisfactory because of poor sensitivity (relative to ethylene diamine) and the least preferred color of yellow. If the toxicity of the diamines proves to be a problem in their use for detection of nitro compounds, it might be necessary to investigate more hydroquinones in an effort to get better results in terms of sensitivity and color reactions in the red to blue region.

The oxidizing action of nitric acid liberated by hydrolysis of the nitrate esters should be detectable by starch-KI by virtue of the liberation of iodine from the KI. Starch is an extremely sensitive indicator for iodine and moreover, the blue color produced will stand out against the color of wrapping paper.

An aqueous solution 2% soluble starch and 2% potassium iodide in water was made up. PETN was dissolved in acetone and spotted on filter paper for the tests.

With starch-KI no color appeared. Irradiation with U.V. gave a negative result as also was obtained on incorporation of benzophenone (a U.V. sensitizer) followed by irradiation.

Starch KI was again added to the dry PETN spots and the paper heated to dryness in an oven at 100 C. No color developed. After a number of attempts, it was concluded that the problem was due to the insolubility of PETN in water. PETN was dissolved in aqueous acetic acid and spotted on paper. After drying the spots, starch KI was applied but no color developed. The paper was reheated, and it was noted this time that the spots showed up pale yellow. When these were moistened with water some blue color developed.

This lead was continued. PETN in aqueous acetic acid was spotted and starch KI added to the spots. Blanks were also run with starch-KI and acetic acid. After drying in the oven at 100 C all gave yellow areas, but on spraying with water the PETN spots were a pronounced blue while the blanks were very pale.

Starch-KI (2%) was diluted with an equal volume of acetic acid and spotted as blanks some of which were treated with PETN in aqueous acetic acid and the paper was dried in the oven and then sprayed with water. The PETN showed up very strongly again and the blanks were negative.

It was found that the starch-KI acetic acid solution became brown overnight. It was also found that on the papers, the blue color did not appear until all traces of acetic acid had been removed prior to the water spray.

It was decided at this stage to try solvents other than acetic acid for admixture with the starch-KI solution. The requirements for the solvent were:

- a. Complete insolubility with starch-KI without precipitation of either
- b. A boiling point high enough so that the solvent remains long enough for decomposition of the nitrate ester to occur
- c. Good solubilizing of PETN (and other nitrate esters)
- d. Not hazardous to personnel or packages to be examined.

Four solvents meeting these requirements are ethylene glycol, glycerol, dimethyl formamide and dimethyl sulfoxide. Of these solvents, glycerol did not work; ethylene glycol gave rather poor sensitivity; and DMF, although giving excellent results, gave a Starch-KI solution which went yellow on standing and also gave slight positives on blanks. DMSO was the best all-around solvent of the ones examined.

Experiments were carried out to determine the optimum amount for admixture with the starch-KI solution. This was found to be 1 vol. of DMSO with 4 vols. of starch-KI, the latter consisting of 2 g KI and 2 g of soluble starch in 100 mls of water.

To determine sensitivity, 100 mg of PETN were dissolved in 100 mls of acetone to give a solution containing 1 mg in 1 ml. 1 ml spots (4 mm in diam) were made on filter paper using a micro syringe and when dry, they were sprayed with the starch-KI DMSO solution (40 mls Starch-KI plus 10 mls DMSO) and evaporated to dryness under a heat lamp. This

took about 2 minutes with the lamp about 5 cms above the paper. At this stage, the PETN spots were clearly visible as yellow spots. The paper was then sprayed with water when the spots immediately turned to a pronounced blue.

Results with the PETN diluted 10 times were negative so that the lower limit of sensitivity is around 1  $\mu$ g.

The reagent easily detected PETN on an envelope which had been sealed by PETN contaminated hands.

It detects dynamite.

The reagent has kept so far for two months with no sign of deterioration and easily detects 1  $\mu$ g of PETN; the blank is completely negative.

We have discovered yet another reagent for nitrate esters which is at least as sensitive as the method above. This reagent, diphenyl amine 1% in alcohol when sprayed on spots of PETN or Dynamite, yields a yellow green spot against a colorless background after exposure to U.V. radiation. After spraying the test spots with the reagent, the papers are exposed to short wavelength ultra violet radiation from a Hanovia high pressure mercury lamp. In 5 to 10 seconds, yellow green spots can be seen corresponding to the explosives. Although a portable U.V. source could be carried along with the aerosol can to the field, it could become burdensome and expensive. The next logical step would be to do away with the U.V. source. What is needed in the system is a photosensitizer to absorb energy at a longer wavelength (visible) and to transfer this energy efficiently to the reacting system. Benzophenone was chosen as such a sensitizer; 0.1% was added to the alcoholic solution of diphenyl amine. The papers were first sprayed and allowed to air dry at room temperature for 1/2 hour. Upon examination no detectable spots could be noted. They were then heated briefly and still gave no spots. It was not until they were exposed to U.V. that any spots appeared.

In an attempt to catalyze the reaction via free radicals, 0.1% of 2,2'-azobis (2-methylpropanitrile) was added to solutions of diphenyl amine.

This compound is thermally cleaved to stable free radicals which could then transfer energy to the reacting diphenyl amine-explosive complex. After warming the papers, no color change could be seen until the papers were exposed to U.V.

Even though the results from these two experiments are discouraging, it seems logical and appropriate to consider investigating this technique more thoroughly. Only two of the possibly hundreds of sensitizers available were tested, and it is feasible that several of these under the proper conditions might act as chemical indicators for these and other explosive compounds and obviate the need for U.V. light exposure.

Another approach, that of using redox indicators, was also briefly investigated. Theoretically, if a reversibly oxidizable compound changes color on going from the reduced form to the oxidized form, there is then a basis for a detection scheme. The nitrocompounds under investigation are all oxidizing agents and therefore are capable of changing the color of redox indicators, provided the indicators have the proper oxidation potential. The result of such a spray system would be a series of spots or streaks corresponding to where the explosive has oxidized the indicator, changing its color. For example, where a compound is colorless in the reduced form and violet when oxidized, spraying with this compound would produce a colorless background with violet spots corresponding to the explosive.

Several representative redox indicators were ordered from Eastman Kodak, Inc. These indicators, their oxidation potential and the color change are listed below:

	Redox Potential	Color Red → Ox
1. N,N-Dimethylindo aniline	0.22	C* → Blue
2. Methylene Blue	0.53	C → Blue
3. Brilliant Cresyl Blue	0.58	C → Blue
4. Diphenyl Amine Sulfonic Acid NaSalt	0.85	C → Violet
5. Naphthol Blue Black	--	Blue → C

\* C = Colorless

	<u>Redox Potential</u>	<u>Color Red → Ox</u>
6. Dibromo Indophenol NaSalt	0.82	C → Blue
7. Dicyano Bis Phenanthroline Iron	1.41	Red → Blue

Solutions were made up of these indicators in alcohol and sprayed on filter papers previously spotted with the explosives. None of the test papers showed significant color change in the areas where explosives had been spotted. Possible additional aspects which could be evaluated in the future are: a) to consider other commercial indicators since only seven of thirty-three Eastman Kodak indicators were checked, b) more polar solvents such as dimethyl formamide and dimethyl sulfoxide could be assessed and c) as in current tests, it would be well to continue to vary such parameters as temperature, pH and the effect of radiation.

### 3. CONCLUSIONS

This study has achieved success in approaching the goals defined at the program outset. It was recognized that a single universal detection substance might be unrealistic, but it was expressed as desirable that a combination of reagents could achieve the objective of detecting classes of explosive compositions. This objective has been met.

The aspects of sensitivity to explosives were subject to definition. No firm data on detection levels were obtainable from government sources; consequently, an assumed objective of 5 microgram detection capability was an unconfirmed goal. The results of this effort demonstrated a sensitivity of 2 micrograms for PETN, and 1 microgram for nitrate esters.

The project has expanded the ground rules for detection, and exploited the freedom to use ultraviolet exposure to detect the reaction with the explosives in question. This in turn leads to the consideration of such complex systems as those which can transfer U.V. response to the visible region, and obtain a signal free of requiring the U.V. exposure.

The question of toxicity has not been resolved, but the matter has been addressed. It has been found that toxicity levels must be defined and confirmed.

It can safely be concluded that this program has demonstrated the feasibility of explosives detection in microgram concentration for the broad range of explosives anticipated. This project was developed to the point where more specific studies are in order. The techniques and reagent systems are ready to be tailored to meet those specific requirements that rise from the consideration of such matters as:

1. Type of paper to be inspected as the composition and the treatment of manufacture will introduce chemicals that may affect the sensitivity of the reagents used.



2. The type of inks to be encountered, since cheap inks are likely to incorporate nitrate lacquers, or nitrocellulose thickeners, substances which would be expected to furnish positive reactions to the detecting sprays.
3. Detection of the use of the reagent, in the case of negative results. The ultimate application of such detection spray may be clandestine in situations where the inspection would be an act to be undisclosed.
4. Effect of reagent on the enclosure. Should the examination be conducted as a part of a customs inspection, the spray must not affect luggage either by attacking the material or by leaving a stain.
5. Toxicity limits. Should the application be a multishot situation, then toxicity requirements will be more stringent than for occasional applications. Hazards may arise from carrier, or from reagent, but the levels to date have not been realistically imposed.
6. Reagent mixtures optimization. To date, the feasibility of such a technique has been of overriding importance. The next phase should address the matter of minimizing reagent concentration and maximizing reagent sensitivity. The exclusivity of the reagents must be tested over a much wider range of materials that might give false positive reactions.

#### 4. RECOMMENDATIONS

Based on results of this study, continuance of this work in several areas is recommended. Firstly, more should be done on ascertaining the mechanism of the diphenylamine-UV reaction.

Only two of the many photosensitizers available were investigated. Theoretically, one could use a photosensitizer or dye which would absorb radiation in the visible portion of the spectra and transfer this energy to the reacting system. When material is thermally decomposed to a stable free radical species, the free radicals then initiate the reaction. Each of these approaches could yield satisfactory results if the reaction mechanism were known.

Also recommended is continuing the work on using the color change of redox indicators, that is, screening several more of these compounds for reaction with explosives and varying experimental conditions such as solvent pH, temperature, catalysts, etc.

Another approach which has not heretofore been mentioned but which might prove quite fruitful is the situ reduction of the explosive compounds to amines and identification of these amines with a spray reagent. There are several reagents which would give a colored product with amine, the most common of which is probably the ninhydrin test for free amino groups. If the explosive could be conveniently reduced, keeping in mind the restrictions set forth in the work statement, this could lead to the most sensitive test to date.

5. REFERENCES

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