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Survey of Candidate Chemistries for Skive Joint Deterioration Indicator Strip

FINAL REPORT

December 31, 1991

Prepared for Product Assurance Directorate
U.S. Army Armament Munitions and Chemical Command
Picatinny Arsenal
Dover, New Jersey 07806-5000

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UCN-7969 (3 9-77)

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This work was sponsored by the U.S. Army Armament Munitions and Chemical Command, under U.S. Department of Energy contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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Executive Summary

Predictive surveillance can improve the safety and reliability of munitions in the field and in stockpiles. A technology for identifying munitions liable to failure would considerably facilitate their monitoring. Studies are underway to survey and identify reagent systems which would be good candidates for the development of an indicator strip for impending skive joint or case wall deterioration in the M829 APFSDS kinetic energy round and similar combustible cartridge case munitions. Previous AMCCOM studies have shown that nitroester migration from the propellant and moisture accumulation within the case are major factors which affect the deterioration and performance of the combustible cartridge case wall and adhesive joint. This report presents the exploration and evaluation of potential colorimetric reactions suitable for detecting nitroester migration and case wall moisture.

The indicators must meet several criteria, including compatibility with the nitrocellulose case wall, specificity, durability, and no toxicity or other hazards. After a thorough literature review, we found that there were three fundamental detection methods (nitrite, nitrate, and fluorescence quenching) which appeared promising for indicating nitroesters such as NG (nitroglycerin) and DEGDN (diethyleneglycol dinitrate). NG and DEGDN are energetic components of the JA-2 propellant. The modified Griess reaction (a nitrite method) was tested and found to generate a brilliant red color in response to nitroesters in solution. This reaction was then adapted to a solid state reaction. The two-layer indicator approach appears compatible with the combustible cartridge case. UV - induced diphenylamine blue formation (based on nitrate-specific detection concept) and fluorescence quenching technologies are also found to be promising candidates for indicating nitroesters.

Four inorganic salt indicators ($CuCl_2$, $CuSO_4$, $CoCl_2$, and $NiCl_2$) for moisture were identified. $CuSO_4$ was shown to be a promising moisture - indicator. A technique of inserting a water-permeable barrier between the case wall and the indicator is needed to potentiate its response.

The identification of indicator reactions suggests that indicator strips are feasible. The production of prototype indicator strips will require additional technology development and optimization.

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Introduction

Anecdotal reports of skive joint disbonding or case wall weakening in the M829 APFSDS kinetic energy antitank round suggest the need for technologies for monitoring combustible cartridge case (ccc) munitions. Field monitoring of individual rounds of munitions is needed to supplement field life predictions from modelling and to identify those rounds at risk of premature failure. Round-to-round variability in adhesive joint tensile strength observed in studies of full-up M829s suggests that surveillance at the level of individual rounds is needed to insure munitions reliability.

Previous AMCCOM (1-2), Honeywell (3), and ORNL studies (4) have identified two properties which affect the deterioration and performance of ccc materials and which could form the basis of individual round surveillance. Nitroester migration from the propellant is an essentially irreversible internal effect which contributes to disbonding of the adhesive joint and probably also to the weakening of the case wall material (1). Moisture accumulation within the case also causes softening of the case walls and contributes to improper ignition and incomplete consumption of the ccc material in firing.

A color-change strip (Figure 1) for visually estimating the nitroester and/or moisture content of combustible cartridge case wall at the skive joint would allow the field identification of rounds which are liable to failure. Such rounds could be removed from the field for confirmatory testing and disposal or rebuilding. Color-change strip detection methodology should be a simple, easy, rapid, and cheap field-monitoring technology. Thus,

in this study a thorough survey and evaluation of potential colorimetric reactions systems was conducted in order to identify promising candidates for the development of indicator strips for impending skive joint or case wall failure in the M829 round and other munitions which employ combustible casing and adhesive joints.

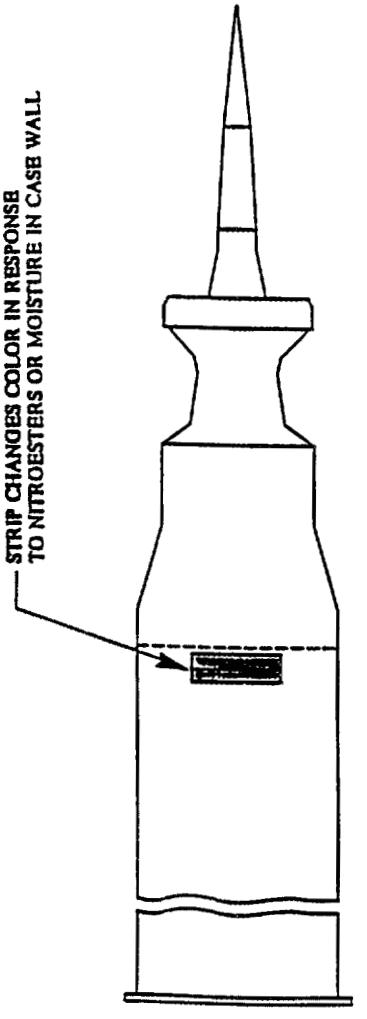

Fig. 1. Skive Joint Indicator Strip Concept

Nitroester-Specific Colorimetric Reagents Study

I. Literature Survey

After a thorough literature review (5-20), we find that there are three fundamental detection concepts which appear promising for indicating nitroesters such as NG (nitroglycerin) and DEGDN (diethyleneglycol dinitrate). NG and DEGDN are energetic components of M829 propellant. The reagents, detection limits, and product colors of trace detection methods found in the literature are summarized as follows:

A. Nitrite Method. Nitroesters can be converted to nitrite by a metallic reduction reagent (such as Zn, Cd, and Hg). Nitrite can be easily identified with one of the following colorimetric reagent systems,

Reagent	Limit of Identification, μg	Product Color
Griess Reagent	0.01	Red
1,8-Naphthylenediamine	0.1	Orange-Red
Iodine + Starch	0.0025	Blue
Chrysean	0.25	Red
Benzidine Acetate	0.7	Yellow-Brown
Safranine T	0.5	Blue
2-Amino-4-Chloromethylthiazole	1.0	Red
m-Phenylenediamine and Cation Exchange Resin	0.04	Orange-Brown

B. Nitrate Method. Nitroesters must first be either hydrolyzed or activated by UV light to form nitrate which can easily react with any of the following colorimetric reagents,

Reagent	Limit of Identification, μg	Product Color
Ferrous Sulfate and H_2SO_4	2.5	Brown
Diphenylamine and H_2SO_4	0.5	Blue
Diphenylbenzidine and H_2SO_4	0.07	Blue
Brucine and H_2SO_4	0.06	Red
Chromotropic Acid and H_2SO_4	0.05	Yellow
Diphenylamine and UV Light	1.0	Yellow-Brown

C. Fluorescence Quenching. The concept of this method is not a chemical reaction but a physical phenomenon. Nitroester compounds on a thin layer chromatography plate coated with silica gel impregnated with a fluorescent indicator (such as manganese-activated zinc silicate) appear as dark spots against a gray-green fluorescent background when illuminated with UV light (254 nm). Incorporation of a silica gel patch impregnated with the fluorescent indicator would allow the nitroesters to be detected by the loss in fluorescence under UV light.

II. Exploratory Study on Selection of Candidate Chemistries for Nitroesters

There is a large body of information for spot tests of nitroester-specific compounds (see above). A systematic evaluation of reaction systems is needed in order to determine and select the most applicable reagents. The selection criteria for the colorimetric chemistries include,

(a) The formation of a product which can be visualized directly or under UV light.

(b) The reaction should be reasonably specific for nitroesters, and provide at least a semiquantitative indication of nitroester content.

(c) The reactions can be conducted in the dry state. Wet-chemical reactions are unsuitable for affixing to a round.

(d) The chemistry should not require strong oxidizing agents or extremes of pH, to avoid damaging the round.

A. Nitrite Method. Since most spot tests for nitrites reported in the literature are carried out in wet-chemistry systems, our evaluation of nitroesters by the nitrite method will first follow this approach. Promising reaction systems will then be conducted upon solid media such as filter paper. NG and DEGDN in aqueous solutions with zinc and each of the above mentioned nitrite-specific systems were qualitatively tested. The results showed that only the Griess reagent indicated a positive color change. It is interesting to note that in the literature, among all the nitrite-specific reagents only the Griess reagent

(consists of sulfanilic acid and 1-naphthylamine) has been mentioned to be sensitive for detection of explosives containing nitric acid esters (5). In the Griess reaction system, nitroesters are first reduced to nitrous acid with zinc metal in an acidic medium (sulfanilic acid). The nitrous acid reacts with a primary amine (sulfanilic acid) to produce a diazonium cation which then reacts with another primary amine (1-naphthylamine) to form a purple to red colored amino azo compound (Figure 2).

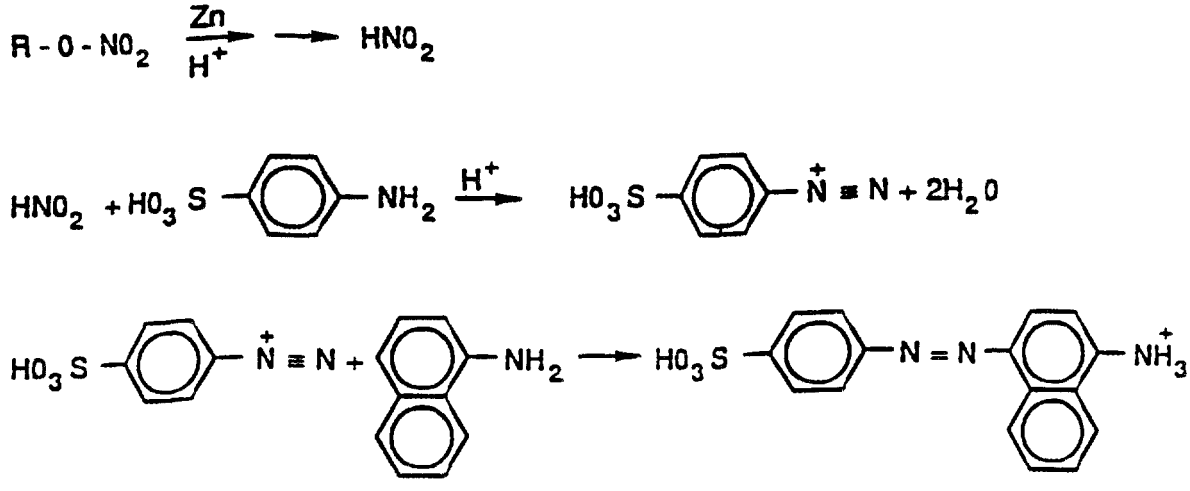

Figure 2. Formation of Colored Dye from a Nitroester by the Griess Reaction

Cd and Hg are also reported to be used as reducing metals for nitroesters. Because of their toxicities we feel these reagents are not suitable for field use. The quantitative determination of NG or DEGDN in aqueous solution by the Griess reaction also was tested. The reaction was conducted by using 4 mL of standard Griess reagent solution and 1 mL of 0, 1, 5, 25, and 125 ppm of either NG or DEGDN. The results are illustrated in Figure 3. Both NG and DEGDN can be readily detected by a light purple color in the 1 ppm range by this reaction. It is interesting to note that when the concentration of NG is increased to 25 ppm, the solution color turns to red. Since this azo dye is so sensitive and the reaction conditions are mild (e.g., does not require a strong acid or high temperature), the reaction might be carried out in the solid state, as would be required for an indicator strip. It appears to be a good candidate for an indicator strip chemistry. The detailed development of an indicator strip based on the Griess reagent system is described in the following section.

In the literature survey section, we noted that starch/iodine is more sensitive (see above) than the Griess reagent for detecting nitrite compounds. But no color was observed if nitroesters were mixed with zinc, starch, and KI in aqueous solution. In a further investigation, we have found that a blue color formation was observed in a commercially available starch/iodine paper strip when it was dipped into aqueous DEGDN solution (100 μg/mL concentration) containing zinc dust and tartaric acid. Without the tartaric acid, no color formation was indicated. This might suggest that nitrite (converted from DEGDN by zinc) should first form nitrous acid (induced by tartaric acid) which might

have a sufficient oxidation potential to oxidize iodide to iodine which then reacts with starch to form the blue color. Sulfanilic acid (a component of the Griess reagent) also was tested in place of tartaric acid, but no blue color was observed. To determine the applicability of this color formation test by starch/iodine paper strip in a solid state system, we have conducted the following experiment. Three commercially available starch/iodine indicator strips were placed in a glass dish. Each strip was only treated with a drop of water, or tartaric acid solution, or zinc/tartaric acid suspension. After 5 min, a blue color formation was observed in the latter two strips. That means that without nitroesters, tartaric acid alone can react with starch/iodine, and that this system has no potential for specifically detecting nitroesters.

Fig. 3. Nitroglycerin (NG) and Diethyleneglycol Dinitrate (DEGDN) in Aqueous Solutions with Zinc and Griess Reagent

B. Nitrate Method. Among all the nitrate methods (see above), the diphenylamine/UV light system is the only approach which does not require the use of a strong acid (such as H_2SO_4) which would damage the M829 case wall. Initial tests of this reaction in the solid state were very promising. In the experiment illustrated in Figure 4 (see page 11), a drop of DEGDN-containing solution was placed on the left side and middle of a piece of Whatman No. 41 filter paper. Then, a drop of diphenylamine-containing solution was placed in the middle and also the right of the filter paper. The solvents were evaporated under a nitrogen stream, and the paper was exposed with 254 nm UV light for 5 min. Figure 4 clearly shows that DEGDN reacts with diphenylamine under UV light exposure to form a brown-yellow product, whereas DEGDN and diphenylamine alone do not. The colored spot is for approximately 20 μg of DEGDN. The detection limit can be much lower. The mechanism of this reaction is still not understood, (see Fig. 5 below) and the color formation is different from that achieved in a strong acid (with nitroester and diphenylamine).

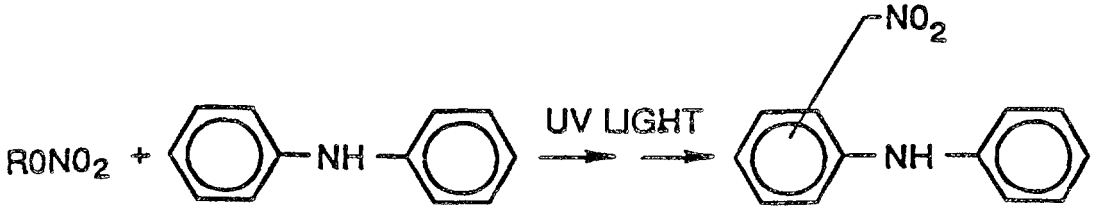

Fig. 5. Hypothesized Diphenylamine Reaction with Nitroesters in the Presence of UV Light.

Fig. 4. Reaction of DEGDN with Diphenylamine in the Presence of UV-Light

C. Fluorescence Quenching. Manganese-activated zinc (which has an activation peak at 254 nm), a commercially available fluorescence indicator produced by Brinkman, can be applied for detecting nitroesters which are expected to quench fluorescence. Initially, we attempted to prepare filter paper evenly-impregnated with manganese-activated zinc silicate, but did not succeed. The problem was due to insufficient fluorescence indicator (obtained by scraping from a Brinkman thin layer chromatography plate). It is very important to prepare an evenly-impregnated filter paper prior to detection of the fluorescence quenching effect of the nitroesters, because an uneven surface causes an interfering uneven fluorescent background. The lack of in-house technology for the preparation of filter paper evenly impregnated with the fluorescence indicator was not critical since the main focus of this experiment was to determine the applicability of the concept of the proposed detection method. Therefore, a glass plate evenly coated with manganese-activated zinc silicate (thin layer chromatography plate commercially available from Brinkman) was directly used for the evaluation. This coated glass plate was spiked with 50 μg of DEGDN. Under UV light, a strong blue quenching ring was observed against a bright fluorescing background (see Figure 6). This approach has the advantage that it is not expected to be sensitive to oxides of nitrogen from propellant aging, and the reagents should be very stable and non-toxic. However, it would be the least convenient because it requires the use of an UV lamp to observe the fluorescence. It may be more appropriate technology for the Quality Assurance Specialist in Ammunition Surveillance than for tank crews.

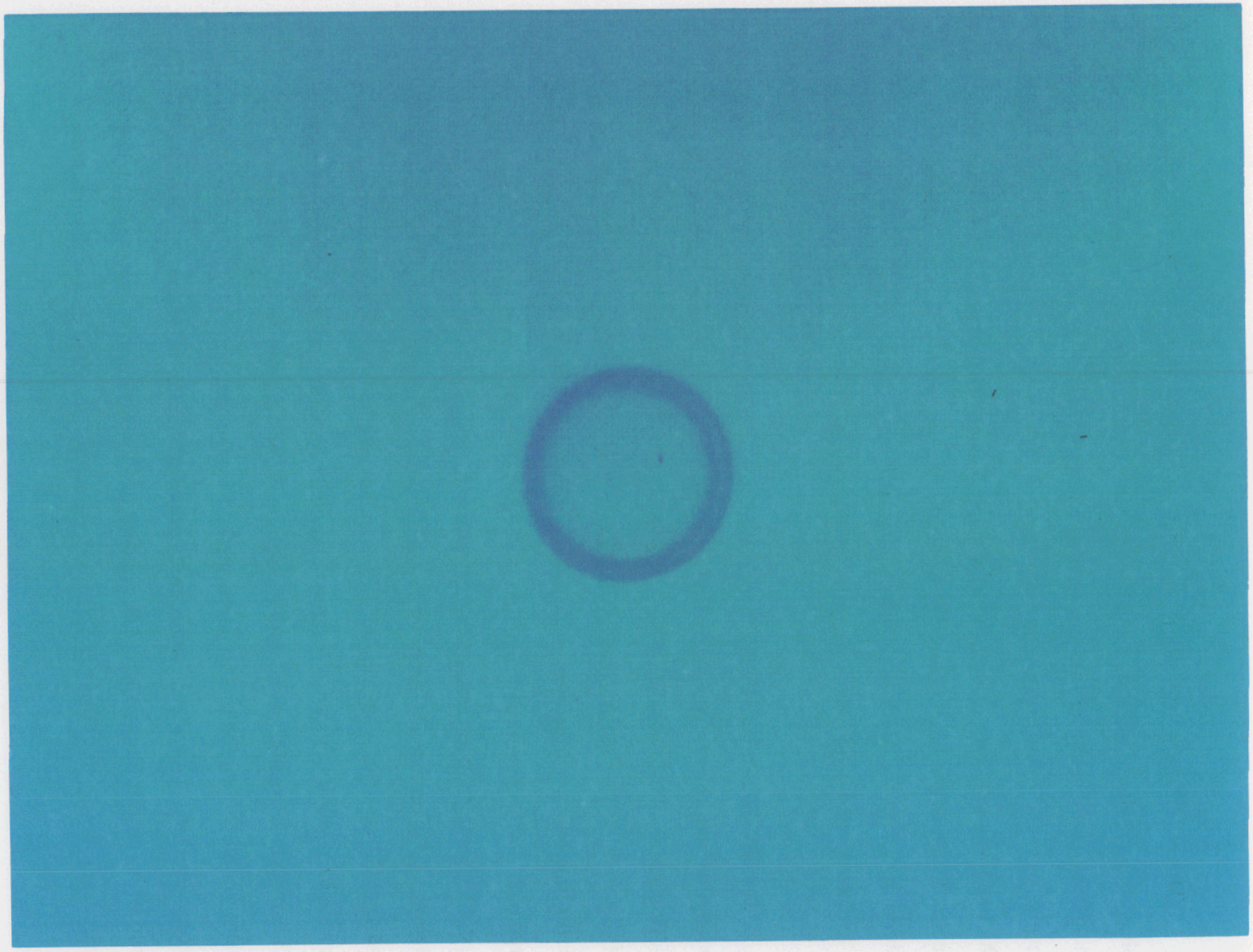

Fig. 6 DEGDN-Fluorescence Quenching on a Manganese-Activated Zinc Silicate Plate

III. Development of Promising Solid State Indicator Strip

Three different detection methods (Azo-dye formation Griess reaction, diphenylamine blue formation, and fluorescence quenching) all appeared promising candidates for indicating nitroesters such as NG or DEGDN in case wall material (see above). However, following the suggestion from the TMAS in our briefing on January 25, 1990, the developmental work of the solid state indicator strip was focused only on color reactions (such as the Griess reaction) which do not require UV light or other activators to develop or visualize the color. Simplicity of use by the tank crew appeared to be the key feature desired in an indicator system, and this eliminated two of the three candidates.

Initially, we qualitatively investigated solid state reactions on filter paper impregnated with the Griess reagent and zinc dust for detection of nitroesters. No clear azo-dye color formation was observed. The negative results were due to one or more of the following reasons: (1) the concentration of nitroesters was too low (ca. 5 μg), (2) the reaction time was not long enough (10 days), (3) too much zinc dust (a gray color) was impregnated in the paper, and may have obscured detection of the colored azo-dye, (4) unstable 1-naphthylamine turned to light-brown, which may have interfered with the color formation. To overcome the problem caused by the instability of 1-naphthylamine in air, we have explored other reagents and have found that N-(1-naphthyl)ethylene diamine dihydrodichloride salt is a stable, colorless and similarly nitrite-specific reactive compound which can replace 1-naphthylamine in the azo-dye color reaction (6,10,12,14,15,19). The problem of the azo-dye color formation masked by the zinc dust (a gray color) can be overcome by using a two-layer solid state indicator system, in which the zinc dust is covered with another filter paper. The concept of this two-layer indicator system can be illustrated as follows: Two filter papers overlap each other. Zinc dust is placed between

these two filter papers. The upper paper is treated with a modified Griess reagent [sulfanilic acid and N-(1-naphthyl)ethylene diamine dihydrochloride salt] and the lower paper is left untreated. In the literature, this modified Griess reagent is sometimes called Saltzman's reagent (10,14). This two-layer filter paper system could be placed on the M829 case wall at the skive joint (see Figure 1). If nitroesters are present on the case wall, these liquid components can diffuse into the lower filter paper and contact the zinc and the modified Griess reagent, forming the color dye in the upper paper layer.

We have tested this nitroester-specific two-layer solid state indicator concept. Instead of using the real case wall at the skive joint, we placed 10 μg of DEGDN on the lower filter (configured as noted above) and after 2 hours a clear purple color was observed. For each of the three control experiments, in which one of the three components (modified Griess reagent, zinc dust, and nitroester) was absent, no azo dye color formation was observed, demonstrating the specificity of the solid state reaction (see Figure 7). This simulated experiment could be extended into a real case wall experiment.

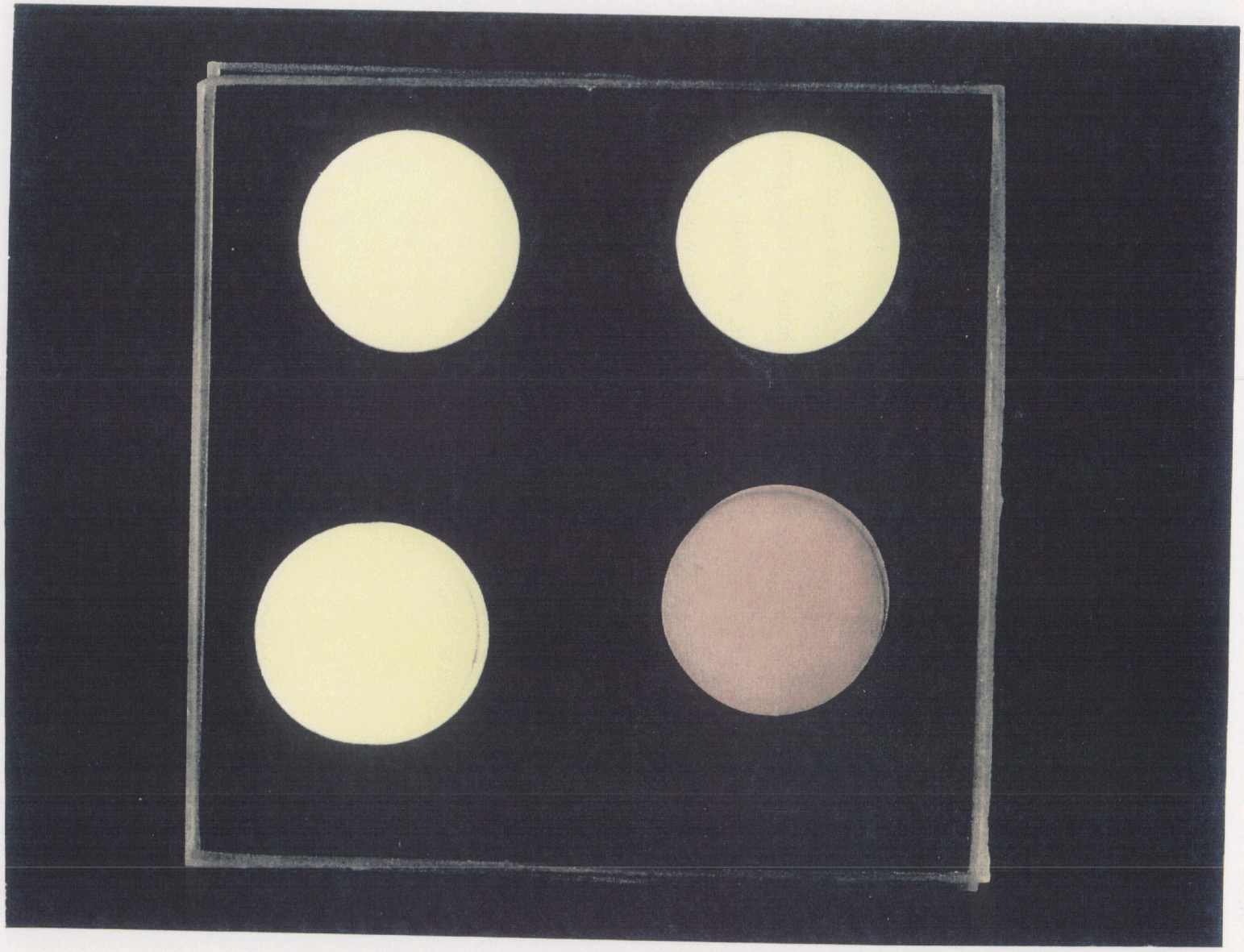

Fig. 7. Detection of DEGDN on a Two-Layer Solid State Indicator Strip. (Only the colored circle contained all reagents plus DEGDN.)

Moisture-Specific Colorimetric Indicators for Combustible Case Wall Study

I. Literature Survey

The concept of a colorimetric indicator relies on chemical systems which can react physically or chemically with water and cause a change of color. We have found in the literature (21) that there are four stable inorganic salts which undergo a distinctive color change during hydration (see Figure 8). The color changes of these four chemicals are as follows:

(1) $CuCl_2$ (brown) + water -- $CuCl_2 \cdot 2H_2O$ (green)

(2) $CuSO_4$ (light blue) + water -- $CuSO_4 \cdot 5H_2O$ (blue)

(3) $CoCl_2$ (lavender) + water -- $CoCl_2 \cdot 6H_2O$ (red)

(4) $NiCl_2$ (yellow) + water -- $NiCl_2 \cdot 6H_2O$ (green)

Evaluation of case wall humidity indicators based on these four inorganic salts is described in the next section.

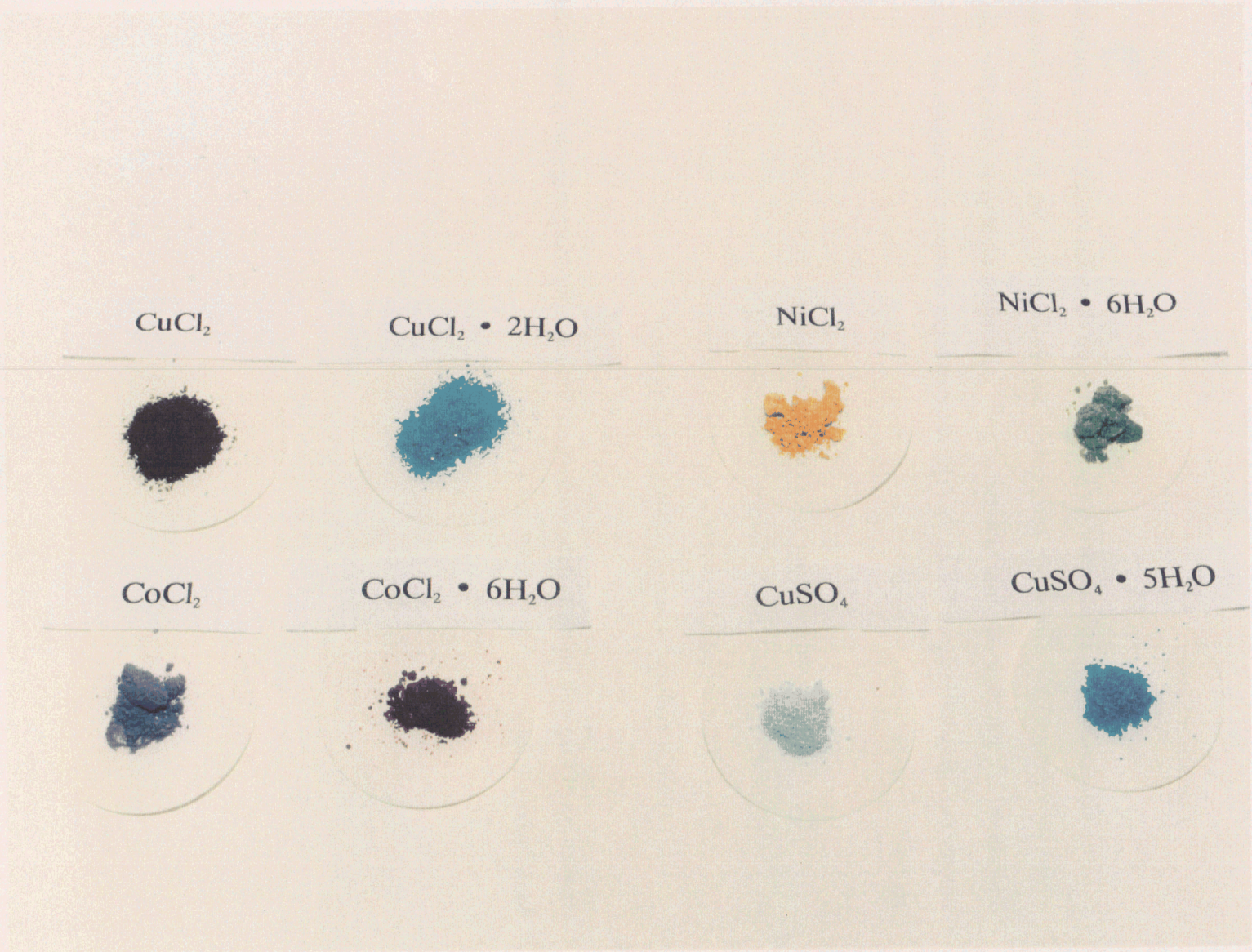

Fig. 8. Color Changes of Inorganic Salts During Hydration

II. Evaluation of Colorimetric Indicators of Combustible Case Wall Moisture

Investigation of four inorganic salts ($CuCl_2$, $CuSO_4$, $CoCl_2$, and $NiCl_2$) as potential indicators of case wall moisture has been conducted. We developed a method for epoxying a clear Teflon "window" over humidity indicators applied to the outside surface of the nitrocellulose portion of combustible case coupons. The four salts listed above, plus "Indicating Drierite" (a commercial desiccant which turns from blue to pink with humidity) were tested. We found that all of the indicators, except for copper sulfate, changed color after an 18 hour exposure to the nitrocellulose at ambient room temperature (ca. 23°C) and humidity (ca. 50% RH). This shows that all (except for copper sulfate) were too sensitive and are unsuitable to indicate case wall moisture at the high concentrations that are of concern. It is possible that placement of a water-permeable barrier between the case wall and the indicators might reduce the sensitivity of the indicators.

Since copper sulfate was observed to be the least sensitive of the inorganic moisture indicators tested (see above), further experiments were conducted with it. We sealed copper sulfate under Teflon windows on the sides of coupons, and exposed the coupons to both high humidity (ca. 100% RH) and to very low humidity (ca. 5% RH) as a control. The indicator exposed to the high humidity began to darken in color noticeably after 4 days of exposure, and after ca. 10 days, it reached its maximum darkening (see Figure 9). We conducted weight measurements to estimate the case wall moisture content at the time of change, but the results probably were complicated by moisture changes in the indicator salt itself. Therefore, we repeated the weight change experiments under identical conditions but without the indicator to gain accurate case wall moisture data. The test showed that the moisture content of the nitrocellulose portion of the coupon is ca. 6% moisture at ambient room conditions (ca. 21°C/50% RH). Similarly, we found that

the copper sulfate indicator darkens at ca. 11% moisture in ca. 10 days exposure of the coupons to 97-100% RH.

To potentiate or moderate the sensitivity of the copper sulfate, we have redesigned the indicator patch to include a semipermeable plastic membrane between the copper sulfate and the case wall. A nonpermeable window (glass) covered the indicator. We found that the plastic membrane did not sufficiently desensitize the indicator, and the color darkened in about the same length of time as without the membrane. Also, the epoxy used to hold the patch together and to the coupon wall disbonded from the nitrocellulose under the high humidity conditions.

A measurement of the maximum concentration of water which the nitrocellulose case wall will absorb at room temperature was made in order to determine the levels of case wall moisture which an indicator would need to respond to. Three coupons with the cellulose adaptor portion removed were dried over a desiccant to measure the "dry weight" before hydration. The coupons were then soaked in distilled water and were periodically reweighed. Hydration and absorption of water occurred slowly. After 24 hours, the moisture content increased to 13.9% of the original dry weight. By 4 days, the moisture had increased to a constant value of only 20.2%. It is clear that the nitrocellulose does not take up large amounts of water, and the kinetics of hydration must be slow. However, this content of water may be sufficient to hinder efficient detonation in the cannon chamber. Water must enter M829 cases through cracks or seams between the base and the case wall or through the adapter/penetrator assembly seam. Penetration through the nitrocellulose wall (the exterior of which is coated in the full-up rounds) itself must be minimal. The inorganic moisture indicators we have surveyed are easily sensitive to this level of moisture.

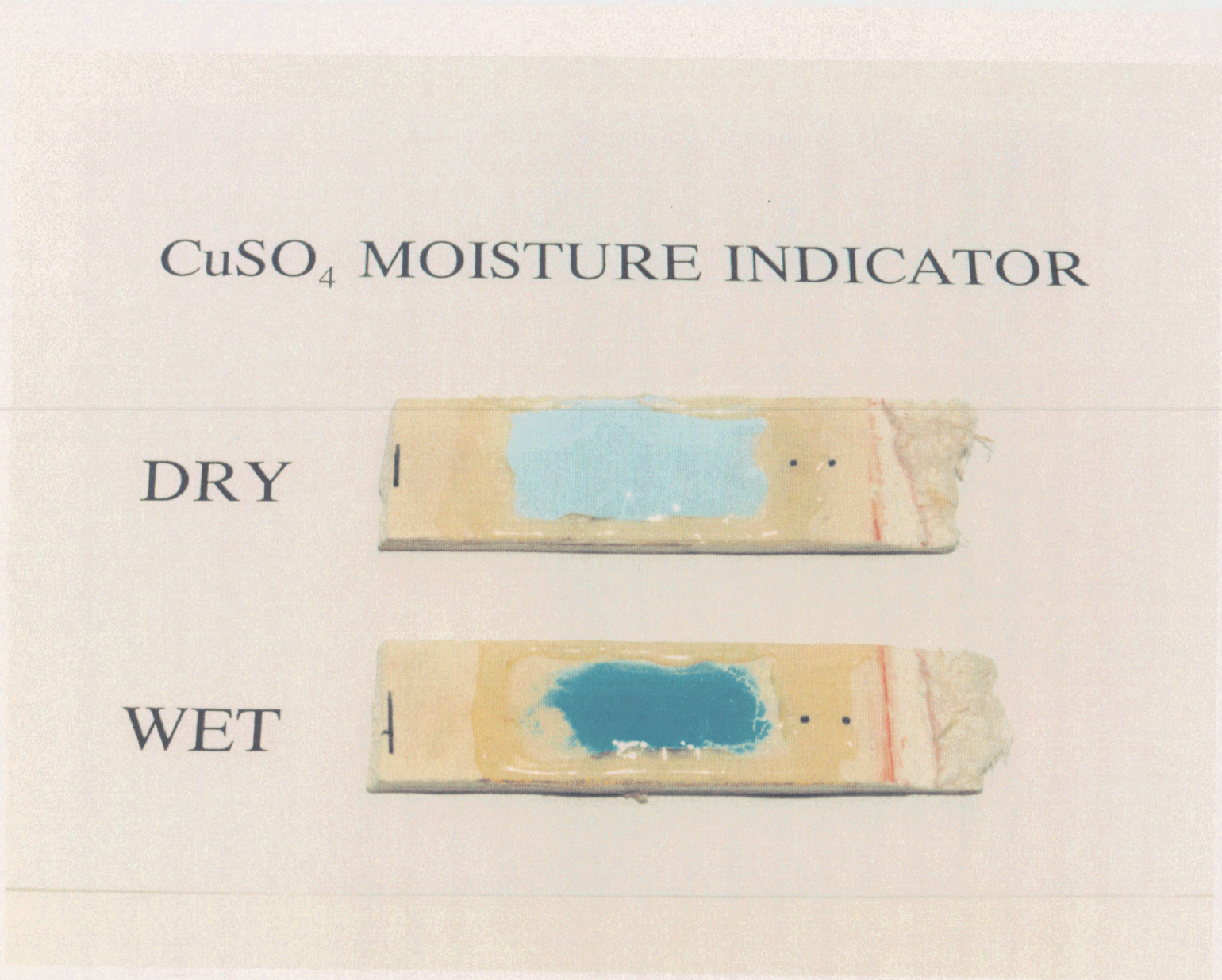

Fig. 9. $CuSO_4$ Moisture Indicator

Summary, Conclusions and Suggestions

The initial work on the exploration and evaluation of potential colorimetric reactions suitable for detecting nitroester migration and case moisture has been completed. The Griess reaction was found to generate a brilliant red color in response to nitroesters in solution, and was adapted to a solid state reaction on the two-layer indicator paper apparently compatible with combustible cartridge case material. N-(1-Naphthyl)ethylene diamine dihydrochloride, a stable compound, was replaced for 1-naphthylamine in the Griess azo-dye color reaction. UV-induced diphenylamine blue formation and fluorescence quenching technologies have also been illustrated to be promising candidates for indicating nitroesters but the requirement of UV light or other activators for the color-visualization hindered their applicabilities. Four inorganic salt indicators ($CuCl_2$, $CuSO_4$, $CoCl_2$, and $NiCl_2$) for moisture were identified. $CuSO_4$ was shown to be a promising moisture-indicator if the technique of inserting a water-permeable barrier between the case wall and the indicator could be developed.

Further work is needed to bring these developments to a state for incorporation into munitions surveillance. Suggestions or proposed work for the development of the color indicator strip to the point where the feasibility of continuing to field testing and industrialization are as follows:

The adaptation of the Griess reaction to the solid state will be tested with coupons doped with nitroglycerin or diethyleneglycoldinitrate (nitroesters in JA-2 and similar propellants) at concentrations identified to cause skive joint failure in our accelerated environmental testing of full-up M829 rounds. The development of a strong, visible color at realistic concentrations must be demonstrated. The stability of the color reaction

reagents and products will be tested in accelerated aging studies, and alternate reagents will be explored if the current chemicals are found lacking. Sensitivity of the indicator reaction to oxides of nitrogen will be investigated to determine if propellant degradation also can be indicated. Finally, preliminary accelerated environmental exposure experiments with full-up M829 rounds will be conducted (if available) to test the behavior of the indicator strips with real munitions. An indicator "band" instead of a strip should be introduced so the indication can be seen from all sides. Inorganic moisture indicators will be tested using coupons. The main problem to be overcome is too great a sensitivity of current indicators, which might be overcome by appropriate barriers or membranes to potentiate sensitivity. Commercially available indicators used in packaging and shipping also will be tested.

In addition, more sophisticated fieldable surveillance technologies (based on state-of-the-art spectroscopy instruments such as optical density monitor, or infrared/near-infrared reflectance spectrometers) also are needed to supplement predictive surveillance of combustible cartridge case munitions in future work.

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