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Color Tests for Diphenylamine Stabilizer and Related Compounds in Smokeless Gunpowder

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ABSTRACT: Reagents containing sulfuric acid commonly used in forensic science laboratories for drug testing have an application as well for the characterization of smokeless gunpowders. Sulfuric acid, alone or with modifying materials, will react with diphenylamine stabilizer to give a considerable degree of intraclass variation among smokeless gunpowders.

KEYWORDS: criminalistics, chemical analysis, diphenylamine, gunpowder

In connection with its work on a mass spectrometry approach to the analysis of gunshot residues, the FBI laboratory has compiled an array of 23 organic compounds that may occur in smokeless gunpowders.[2] These compounds are listed in Table 1. Nitrocellulose will invariably occur. Nitroglycerin will occur in all double-base gunpowders. The presence of other organic compounds is variable; different explosive materials and stabilizers are added according to the manufacturer's specifications as predicted by performance and economic considerations.

Diphenylamine (DPA) appears on the FBI's list of organic compounds occurring in smokeless gunpowders. As early as 1909, DPA was being used in the United States, France, and Germany as a stabilizer for smokeless gunpowders [*1*]. Typical bulk gunpowders contain from 0.51 to 0.89% DPA, which limits nitrocellulose decomposition arising from exposure to the acid products of that decomposition [*1,2*].

Since around 1872, the presence of nitrates has been determined by using DPA in analytical procedures.[3] In 1911, Wellenstein and Krober used DPA in the presence of concentrated sulfuric acid as a reagent for nitrate detection.[4] Curiously, brucine in the presence of concentrated sulfuric acid was initially considered more specific toward nitrates. For reasons that are no longer recoverable, however, the test has been relegated to obscurity [*3*].

Diphenylamine has a unique and somewhat checkered past in forensic science work. The

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[2]D. Hardy, FBI Laboratory, personal communication, 1979.

[3]F. Fitzpatrick, Forensic Science Group, University of California at Berkeley, personal communication, 1973.

[4]F. Fitzpatrick, Forensic Science Group, University of California at Berkeley, personal communication, 1973.

TABLE 1—*Organic compounds that may be found in smokeless gunpowder.*

Cresol	RDX (Cyclonite)
Resorcinol	Diethyl phthalate
Carbazole	Nitroglycerin
Diphenylamine	Trinitrotoluene
Dimethyl phthalate	Dimethylsebacate
N-Nitrosodiphenylamine	*N*,*N*-Dimethylcarbanilide (Methylcentralite)
Dinitrocresol	2,4-Dinitrodiphenylamine
Carbanilide	*N*,*N*-Diethylcarbanilide (Ethylcentralite)
Nitrodiphenylamine	Dibutyl phthalate
Triacetin	PETN (Pentaerythritol Tetranitrate)
Nitrocellulose	*N*,*N*-Dibutylcarbanilide (Butylcentralite)
Nitrotoluene	

DPA test for nitrates formed the basis for the "dermal nitrate" or "Gonzales" test introduced in 1933 as a test for gunshot residues [*4*]. This test has been discredited as a test for determining whether a person has fired a weapon because nitrates are ubiquitous in the environment and because there is no differentiation between nitrates from gunpowder and those from other sources [*2,5,6*]. These interfering factors, which may cause false positives, are tobacco ash, pharmaceuticals, fertilizers, leguminous plants, urine, and colored fingernail polishes [*6*]. The DPA test, however, continues to be used, generally as a spot test, to confirm particulate material removed from a target as gunpowder, for example, fragments of suspected gunpowder removed from around a suspected bullet hole in a garment.

In the present work, the initial question regarding this matter was the following: If DPA is already present in some gunpowders, would it be possible to leave DPA out of the DPA reagent, that is, use only concentrated sulfuric acid, and still obtain the blue reaction product observed with the DPA reagent and smokeless gunpowders? This test would be a test not for nitrates but for DPA, and it would discriminate between those gunpowders containing DPA and those that do not. A collateral question was that if this test, using only concentrated sulfuric acid, was able to detect DPA in gunpowders, would other sulfuric acid-containing reagents commonly used in criminalistics laboratories for the identification of alkaloids provide some discrimination among smokeless gunpowders? A sensitive test for DPA in gunpowder and gunpowder residue is inherently more attractive from a forensic science standpoint than is a test for uniquitous nitrates.

Experimental Procedures

Materials

The color tests were performed with the 34 gunpowders listed in Table 2. The color-forming reagents used [*7*] were the following:

- concentrated sulfuric acid (H_2SO_4), 17.8*M*;
- concentrated nitric acid (HNO_3), 15.4*M*;
- Mandelin, formed by dissolving 5% ammonium vanadate (NH_4VO_3) in concentrated sulfuric acid; the solid should be finely ground to promote suspension;
- Rosenthaler-Turk, formed by dissolving 0.1 g of potassium arsenate ($KH_2As_5O_4$) in 10 mL of concentrated sulfuric acid;
- Frohde, formed by dissolving 1 g of ammonium molybdate [$(NH_4)_2MoO_4$] in 10 mL of concentrated sulfuric acid; this solution should be clear and it is not stable;
- Marquis, formed by adding three drops of 40% formaldehyde solution to 3 mL of concentrated sulfuric acid;

- Wasicky, formed by dissolving 2 g of *p*-dimethylaminobenzaldehyde in 6 g of concentrated sulfuric acid;
- Schaer, formed by dissolving 0.1 mL of reagent-grade 30% hydrogen peroxide (H_2O_2) in 1 mL of concentrated sulfuric acid; this reagent must be fresh; and
- Mecke, formed by dissolving 5 mg of selenious acid (H_2SeO_3) in 1 mL of concentrated sulfuric acid.

The chemicals tested were *N,N*-diphenylamine (DPA) (ICN Pharmaceuticals, Inc., Plainview, NY) and *N*-nitrosodiphenylamine (DPNA) (ICN Pharmaceuticals, Inc.).

Method

Three series of tests were performed on the various gunpowders and chemicals.

The first series involved characterizing the nature of the color reactions, utilizing whole gunpowder particles and the various sulfuric acid-containing reagents. Three particles of each of the 34 gunpowders were reacted with two drops of the color-forming reagents. These color reactions were observed in a spot tile depression with a Spencer stereomicroscope at 18×. The light source was a Tiyoda tungsten filament lamp adjusted to 6 V. Each color reaction was designated by color according to Inter-Society Color Council-National Bureau of Standards (ISCC-NBS) Color Charts Illustrated with Centroid Colors [*8,9*].

The second series was performed on the various gunpowders and chemicals dissolved in acetone. As in the first tests, three particles of gunpowder were placed in a spot tile depression; then a sufficient quantity of acetone was applied to cover the particles. After the acetone evaporated, two drops of each of the various reagents containing concentrated sulfuric acid were reacted with the dissolved residue. The reactions were observed under fluorescent lighting without magnification. Each reaction was designated by color using the ISCC-NBS Color Charts [*8,9*].

The third series involved determining the sensitivity of the sulfuric acid/nitric acid reagent combinations on DPA, DPNA, and one gunpowder, Hodgdon #375. One gram of each was dissolved in 100 mL of acetone. A series of four further dilutions was made by successively taking 1 mL from the proceeding dilutions and mixing that in 9 mL of acetone. One-half millilitre of each of the serial dilutions was placed in a depression of a spot tile and allowed to evaporate. Each chemical and gunpowder were tested in two ways. First, the reaction was observed when one drop of nitric acid was applied and the color was allowed to form and then one drop of concentrated sulfuric acid was added. Secondly, the reaction was observed when one drop of concentrated sulfuric acid was applied first and then the concentrated nitric acid. A blue color reaction determined the level at which the reagent was most sensitive.

TABLE 2—*Smokeless gunpowder samples tested.*

Alcan	Du Pont	Olin	Hercules	Hodgdon	Norma
101	3031	WC 230	Herco 110	375	204
5	4198	WC 235	Herco 210	380	
7	4227	WC 530 D	2400	570	
8	4320	WC 630	Red Dot 10	870	
	4350	WC 680	Red Dot 90	H 4227	
	4759	WC 748		H 4831	
	4831	450 LS		HS-10	
	Hi-Skor			BLC 2	
	#6 Pistol			4895	
	#18				

Results

An analysis of the results of the first series of tests showed an immediate, distinctive, and persistent color reaction with similarities in hue among the eight reagent/gunpowder color reactions, as seen in Table 3. Certain exceptions can be noted, especially with Wasicky's reagent. This deviation in hue down the column is due to the inherent color of the reagent (55 s.Br), which masks all but one of the color reactions; therefore, it was excluded from any subsequent tests. Other exceptions can be noted along the rows, but these are not as consistent as the color reactions seen with Wasicky's down the column. Contrary to the premise of this experiment, only Hodgdon #375 reacted to give the expected blue color (179 deep B) and was observed only with Frohde's, Marquis', Wasicky's, Schaer's, and Mecke's reagents, with the blue appearing at the periphery of the spot tile depression after 15 to 30 s. This does not preclude the other observed color reactions from being used in the characterization of gunpowder samples.

The second series was performed because of the lack of more positive color reactions in the first series of tests. It was hypothesized that more DPA would be released from the pellet matrix to react with the color-forming reagents if the gunpowders were dissolved in acetone. As can be seen in Table 4, that hypothesis was proved. All positive reactions (ones with the characteristic blue) were given number designations, which are explained at the bottom of Table 4. Negative tests were given their ISCC-NBS color designations. Only Alcan #101, Du Pont #4198, and Hodgdon #4895 failed to give the expected color reaction, possibly because of the substitution of DPA for another stabilizer in the manufacturing process or the presence of a nitro derivative of DPA.

Since the premise of this experiment was proven correct, the next step was to determine the sensitivity of the reaction of concentrated sulfuric acid reacted with DPA, DPNA, and Hodgdon #375. These two chemicals and the gunpowder were chosen because they react with specificity toward sulfuric acid, giving the characteristic blue. Using serial dilutions of 5×10^{-3}, 5×10^{-4}, 5×10^{-6}, and 5×10^{-7} g/L, it was possible to detect 5 μg of DPA, 5 μg of DPNA, and 50 μg of Hodgdon #375 when the dilutions were tested with one drop of nitric acid followed by one drop of concentrated sulfuric acid. When the dilutions were tested with one drop of concentrated sulfuric acid followed by one drop of nitric acid, it was possible to detect 5 μg of DPA, 50 μg of DPNA, and 50 μg of Hodgdon #375.

From this last series of tests, it was determined that it is not necessary to nitrate the samples by adding nitric acid since the characteristic blue was observed without its addition. Another reason, confirmed by Feigl [*10*], is that nitric acid can be used as a color test for secondary amines giving a blue reaction product that varies in intensity according to the amount of reactant present. In forensic science determinations, this procedure should not be used because of its lack of specificity and because it may mask the slightly different color reaction produced by a positive sulfuric acid/nitrate/DPA test.

Discussion

Uses and Methods of Detection of DPA

Diarylamines such as DPA are used as stabilizers not only for gunpowders and explosives but also for polymers, as antioxidants and antiozonants for rubber products and elastomers, as dye intermediates, and as preservatives to prevent storage scald in apples and pears [*11*]. Methods for the determination of DPA and its derivatives can be found in a wide variety of literature: steam distillation; infrared and ultraviolet absorption; nuclear magnetic resonance spectroscopy; paper, thin-layer and high pressure liquid chromatography; X-ray diffraction; and spot testing [*11*].[5] Cook [*12*] has proposed four methods for the determination

[5]L. Haag, Police Crime Laboratory, Phoenix, AZ, personal communication, 1980.

TABLE 3—*Reactions of reagents containing sulfuric acid with solid gunpowder.*

Gunpowder	H_2SO_4 (clear)	Mandelin (66 v.OY)	Rosenthaler-Turk (clear)	Frohde (clear)	Marquis (clear)	Wasicky (55 s.Br)	Schear (clear)	Mecke (clear)
Alcan								
101	57 l.Br	clear	73 p.OY	73 p.OY	73 p.OY	clear	73 p.OY	73 p.OY
5	95 m.OlBr	96 d.OlBr	95 m.OlBr	96 d.OlBr	96 d.OlBr	267 Black	96 d.OlBr	96 d.OlBr
7	95 m.OlBr	95 m.OlBr	84 s.Y	96 d.OlBr	96 d.OlBr	96 d.OlBr	96 d.OlBr	96 d.OlBr
8	84 s.Y	84 s.Y	84 s.Y	84 s.Y	84 s.Y	112 l.OlGy	84 s.Y	84 s.Y
Du Pont								
3031	67 brill.OY	74 s.yBr	56 deep Br	74 s.yBr	74 s.yBr	266 d.Gy	74 s.yBr	74 s.yBr
4198	74 s.yBr	75 deep yBr	75 deep yBr	66 v.OY	66 v.OY	266 d.Gy	66 v.OY	66 v.OY
4227	82 v.Y	267 Black	107 m.Ol	107 m.Ol	108 d.Ol	266 d.Gy	107 m.Ol	111 d.gy.Ol
4320	84 s.Y	66 v.OY	84 s.Y	84 s.Y	84 s.Y	266 d.Gy	84 s.Y	84 s.Y
4350	267 Black	74 s.yBr	77 m.yBr	74 s.yBr	75 deep yBr	266 d.Gy	74 s.yBr	75 deep yBr
4759	86 l.Y	86 l.Y	86 l.Y	86 l.Y	86 l.Y	87 m.Y	86 l.Y	84 s.Y
4831	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black
Hi-Skor	105 gy.gY	105 gy.gY	105 gy.gY	97 v.gY	105 gy.gY	105 gy.Gy	105 gy.gY	105 gy.gY
#6 Pistol	105 gy.gY	83 brill.Y	105 gy.gY	105 gy.gY	105 gy.gY	264 l.Gy	105 gy.gY	105 gy.gY
#18	74 s.yBr	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black
Olin								
WC 230	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black
WC 235	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black
WC 530D	89 p.Y	267 Black	84 s.Y	267 Black	90 gy.Y	266 d.Gy	267 Black	89 p.Y
WC 680	88 d.Y	84 s.Y	87 m.Y	87 m.Y	87 m.Y	266 d.Gy	85 deep Y	85 deep Y
WC 748	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black
450 LS	99 s.gY	267 Black	108 d.Ol	107 m.Ol	108 d.Ol	266 d.Gy	107 m.Ol	106 l.Ol
Hercules								
Herco 110	101 l.gY	84 s.Y	101 l.gY	43 m.rBr	101 l.gY	266 d.Gy	102 m.Gy	102 m.gY
Herco 210	40 s.rBr	51 deep O	53 m.O	53 m.O	50 s.O	266 d.Gy	54 brO	54 brO
2400	98 brill.gY	104 p.gY	102 m.gY	104 p.gY	119 l.YG	266 d.Gy	119 l.YG	119 l.YG
Red Dot 10	105 gy.gY	102 m.gY	102 m.gY	102 m.gY	90 gy.Y	266 d.Gy	104 p.gY	105 gy.gY
Red Dot 90	53 m.O	54 BrO	52 l.O	52 l.O	51 deep O	266 d.Gy	51 deep O	51 deep O

Hodgdon								
375	107 m.Ol	95 m.OlBr	95 m.OlBr	179 deep B[a]	179 deep B[a]	179 deep B[a]	179 deep B[a]	179 deep B
380	102 m.gY	99 s.gY	102 m.gY	102 m.gY	102 m.gY	102 m.gY	102 m.gY	102 m.gY
570	94 l.OlBr	94 l.OlBr	91 d.gy.Y	91 d.gy.Y	91 d.gy.Y	266 d.Gy	91 d.gy.Y	91 d.gy.Y
870	106 l.Ol	99 s.gY	99 s.gY	99 s.gY	99 s.gY	265 med.Gy	99 s.gY	99 s.gY
H4227	105 gy.gY	105 gy.gY	105 gy.gY	105 gy.gY	105 gy.gY	265 med.Gy	105 gy.gY	105 gy.g
H4831	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black	267 Black
HS-10	102 m.Gy	85 deep Y	102 m.gY	105 gy.gY	105 p.gY	265 med.Gy	105 gy.gY	102 m.gY
BLC 2	97 v.gY	104 p.gY	97 v.gY	97 v.gY	99 s.gY	109 l.gy.Ol	97 v.gY	99 s.gY
4895	51 deep O	51 deep O	51 deep O	51 deep O	50 s.O	266 d.Gy	51 deep O	50 s.O

ISCC-NBS COLOR DESIGNATIONS

40 s.rBr	strong reddish Brown	82 v.Y	vivid Yellow	104 p.gY	pale greenish Yellow
43 m.rBr	moderate reddish Brown	84 s.Y	strong Yellow	105 gy.gY	grayish greenish Yellow
		85 deep Y	deep Yellow	106 l.Ol	light Olive
50 s.O	strong Orange	86 l.Y	light Yellow	107 m.Ol	moderate Olive
51 deep O	deep Orange	87 m.Y	moderate Yellow	108 d.Ol	dark Olive
52 l.O	light Orange	89 p.Y	pale Yellow	109 l.gy.Ol	light grayish Olive
53 m.O	moderate Orange				
54 brO	brownish Orange	90 gy.Y	grayish yellow	111 d.gy.Ol	dark grayish Olive
56 deep Br	deep Brown	91 d.gy.Y	dark grayish Yellow	112 l.OlGy	light Olive Gray
57 l.Br	light Brown	94 l.OlBr	light Olive Brown	119 l.YG	light Yellow Green
		95 m.OlBr	moderate Olive Brown		
66 v.Oy	vivid Orange yellow	96 d.OlBr	dark Olive Brown	179 deep B	deep Blue
67 brill.Oy	brilliant Orange yellow	97 v.gY	vivid greenish Yellow		
73 p.Oy	pale Orange yellow	98 brill.gY	brilliant greenish Yellow	264 l.Gy	light Gray
74 s.yBr	strong yellowish Brown	99 s.gY	strong greenish Yellow	265 med.Gy	medium Gray
75 deep yBr	deep yellowish Brown			266 d.Gy	dark Gray
77 m.yBr	moderate yellowish Brown	101 l.gY	light greenish Yellow	267 Black	Black
		102 m.gY	moderate greenish Yellow		

[a]179 deep B develops after 15 to 30 s. Initial color 95 m.OlBr.

TABLE 4—*Reactions of reagents containing sulfuric acid with the residue of gunpowder dissolved in acetone following evaporation of the solvent.*[a]

Gunpowder	H_2SO_4; HNO_3	HNO_3; H_2SO_4	Mandelin	Rosenthaler-Turk	Frohde	Marquis	Schacr	Mecke
Alcan								
101	clear	clear	82 v.Y	clear	clear	clear	clear	clear
7	1	1	5	2	1	2	2	1
Du Pont								
3031	3	4	5	2	3	3	3	1
4198	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y
4227	clear	clear	5	1	1	1	1	1
4320	3	4	5	2	3	3	1	3
4350	3	4	5	3	3	3	3	3
4759	3	4	5	3	3	3	3	3
4831	3	4	5	3	3	3	3	3
Hi-Skor	3	4	5	8	3	3	3	3
#18	3	4	5	3	3	3	3	3
Bulk 5093	3	4	5	3	3	3	3	3
Olin								
WC 230	3	4	3	3	3	3	3	3
WC 235	3	4	3	3	3	3	3	3
WC 530D	3	4	5	3	3	3	3	3
WC 680	3	4	5	3	3	3	3	3
WC 748	3	4	5	3	3	3	3	3
450 LS	3	4	5	3	3	3	3	3

Hercules								
Herco 110	3	4	5	3	3	3	3	3
Herco 210	3	4	5	3	3	3	3	3
2400	3	4	6	3	3	3	3	3
Red Dot 10	3	4	5	3	3	3	3	3
Red Dot 90	3	4	5	3	3	3	3	3
Norma 204	3	4	7	3	3	3	3	3
Hodgdon								
375	3	4	7	3	3	8	3	3
380	3	4	7	3	3	8	3	3
579	3	4	7	3	3	8	3	3
870	3	4	7	3	3	8	3	8
H4227	3	4	7	3	3	3	3	3
H4831	3	4	7	3	3	3	3	3
HS-10	3	4	7	3	3	8	3	3
BLC 2	3	4	7	3	3	3	3	3
4895	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.Y	83 brill.

[a]Number designations:

1. 179 deep Blue band near the top of the spot plate depression arising from the evaporation of the acetone.
2. 266 vivid pale Purple liquid with the 179 deep Blue band described in Number 1.
3. 237 strong reddish Purple liquid with the 179 deep Blue band described in Number 1.
4. 237 strong reddish Purple liquid with a 183 dark blue band near the top of the spot plate depression arising from the evaporation of the acetone.
5. 84 strong Yellow liquid with the 179 deep Blue band described in Number 1.
6. 51 deep Orange liquid with the 179 deep Blue band described in Number 1.
7. 75 deep yellowish Brown liquid with the 179 deep Blue band described in Number 1.
8. 183 deep Blue liquid with no band.

of DPA and its derivatives in gunpowder and explosives, namely, nitration, soda distillation, extraction, and volumetric analysis. Coldwell [13] has proposed using short wavelength ultraviolet light that, in the presence of DPA and organic nitrates, produces yellow to yellow-green colors. However, this method lacks specificity and cannot differentiate between nitrates of gunpowder or other origin.

These methods lack many of the advantages found in spot tests, which are instantaneous, easy to perform, sensitive, and specific and produce stable products [14]. Davis and Ashdown [2] experimented with color tests for ten nitro derivatives of DPA. They observed the color reactions for these derivatives with alcoholic solutions of ammonia, sodium hydroxide, and sodium cyanide. When these nitro derivatives were reacted with concentrated sulfuric acid, they noted reaction products ranging in color from reddish violet to blue. Only DPNA reacted with concentrated sulfuric acid to give the characteristic blue color. These findings are one explanation for the plethora of colors observed in the first series of tests with whole gunpowder particles (Table 3) and confirm the results observed in the second and third series of tests (Table 4).

When interpreting the data from Tables 3 and 4, the reader should take note of the possibility of metamerism [15]. Each reaction was viewed with a stereomicroscope using a tungsten filament lamp with a color temperature of approximately 2700 K and was characterized by color according to the ISCC-NBS Color Charts viewed under fluorescent lighting (Norelco 40W Warm White), which has a color temperature of approximately 3500 K [16]. Therefore, the color designated for each reaction, although valid in a comparative sense, may vary from the true color.

Of the other organic constituents found in gunpowders, Cyclonite® (cyclotrimethylene-dinitramine) reacts in the presence of DPA and concentrated sulfuric acid, and carbazole in the presence of nitric acid, giving rise to blue reaction products [1,10].

Chemistry and Mechanisms

As shown in Table 1, a number of transformation products occur from the decomposition of nitrocellulose and the resulting transformation of DPA to DPNA, nitrodiphenylamine, and 2,4-dinitrodiphenylamine. These and the other transformation products shown in Fig. 1 arise from the oxygen in the gunpowder particles combining with nitrogen to form radicals such as NO_2^- (nitrite) and NO_3^- (nitrate).[6] Frey [17] states that "DPA decreases linearly with time at a rate set by the decomposition of nitroglycerin or nitrocellulose." Nitrites, in the presence of sulfuric acid, are oxidized to produce the nitrosonium ion (N^+O), which then reacts in the presence of DPA, by electrophilic attack with replacement of the hydrogen ion (H^+), to form diphenylnitrosamine (DPNA) [18,19].

Nitrates, in the presence of sulfuric acid, give rise to the nitronium ion (N^+O_2) through complex ionization [19,20]. The nitronium ion, acting by electrophilic attack directly on the ring structures of DPA, gives rise to variously substituted dinitrodiphenylamines, trinitrodiphenylamines, and tetranitrodiphenylamines [2,19]. The oxidation of DPA forms a free radical believed to be diphenyl nitric oxide [$(C_6H_5)_2NO$] [11]. Diphenylnitrosamines tend to be formed first; then, as the available DPA is depleted, the amount of variously substituted nitro derivatives of DPA increases [1,17]. It has been shown that the nitration of DPA tends to form trinitro-derivatives [11]. These compounds arising from either nitrosation or nitration of DPA may react in the presence of sulfuric acid to form colored reaction products [2].

Grotz [14] states that "the diphenylamine test takes advantage of the oxidizing ability of the nitrate ion in highly acidic solutions to oxidize the colorless diphenylamine to a colored compound called diphenylbenzidine violet" (DPBV). The mechanism for this reaction can

[6]F. Fitzpatrick, Forensic Science Group, University of California at Berkeley, personal communication, 1973.

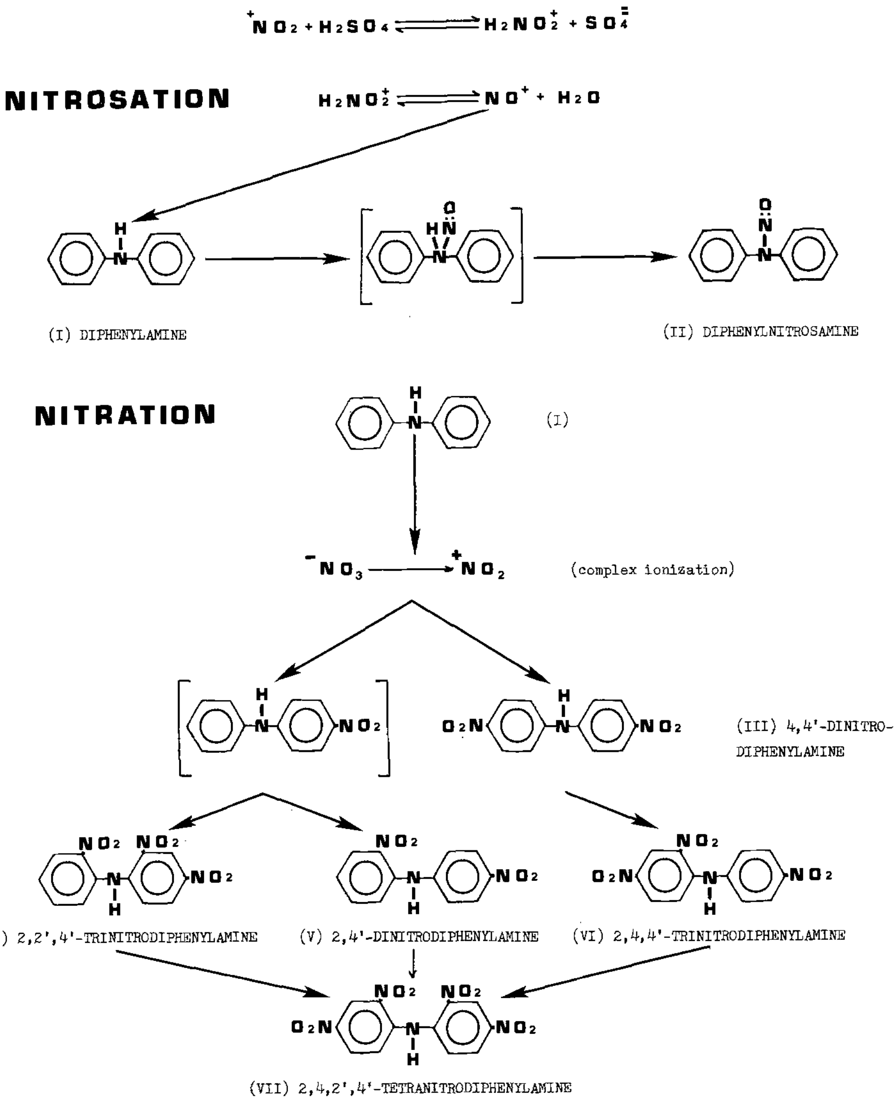

FIG. 1—*Transformation products occurring from the decomposition of nitrocellulose.*

be seen in Fig. 2 and is the subject of an extensive review by Bishop [*21*,*22*]. In the presence of concentrated sulfuric acid and nitrates, DPA is irreversibly oxidized to diphenylbenzidine (DPB), which is then reversibly oxidized to the colored reaction product, DPBV [*21*]. A green intermediate reaction product is often observed between the reduced and oxidized forms of DPB [*21*]. Diphenylbenzidine violet may be irreversibly destroyed by further oxidation to give a yellow or yellow-green insoluble product of unknown composition [*21*]. The reaction will proceed with any of the compounds shown in Fig. 1 as long as there is a free para position and the compound is not meta directed. Therefore, the transformation products, which may react with the sulfuric acid reagent to form the characteristic blue reaction products, are DPA and DPNA. This fact was borne out in the three series of tests performed in this experiment. Any transformation products generated through nitration will not react to form DPBV.

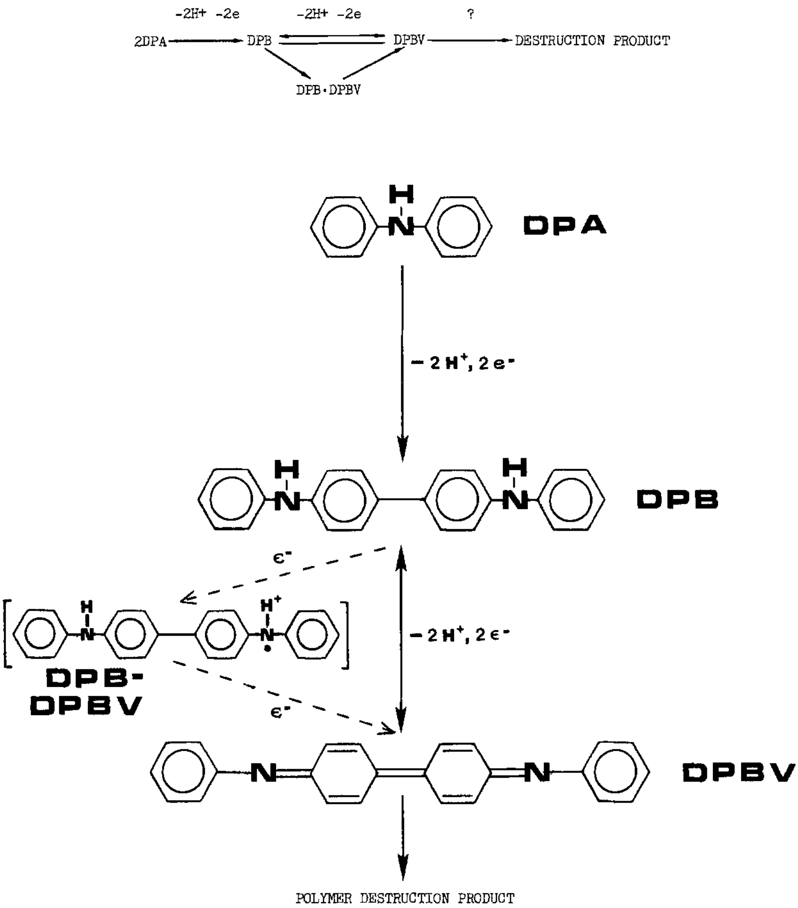

FIG. 2—*Mechanism for the oxidation of diphenylamine to diphenylbenzidine violet.*

This study has shown that sulfuric acid in the presence of nitrates can detect minute quantities of DPA-like materials present in a gunpowder particle. Since some nitrates and nitrites will always be swept along with the explosive gases of a gunshot (approximately 5 to 15% in the form of unburned particles), it is possible that some will be deposited on the hands of the shooter [*23*].[7] If so, it should be possible to detect any DPA and DPNA that may be contained in these particles.

Conclusions

Smokeless gunpowders may be characterized by means of reagents containing sulfuric acid, and those gunpowders containing diphenylamine and its transformation product, diphenylnitrosamine, can be identified by means of a one-step reaction using only sulfuric acid. It was determined that there is no need to nitrate diphenylamine-containing gunpowders first in order to get a positive, blue reaction product.

[7] F. Fitzpatrick, Forensic Science Group, University of California at Berkeley, personal communication, 1973.

A sensitive test for diphenylamine in gunpowder and gunpowder residues is inherently more attractive from a forensic science standpoint than is a test for uniquitous nitrates. The test using only sulfuric acid seems to achieve this aim.

Acknowledgments

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