ROLE OF DIPHENYLAMINE AS A STABILIZER IN PROPELLANTS; ANALYTICAL CHEMISTRY OF DIPHENYLAMINE IN PROPELLANTS (A SURVEY REPORT)

by

Julius B. Apatoff
George Norwitz

December 1973

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Technical Support Directorate

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ROLE OF DIPHENYLAMINE AS A STABILIZER IN PROPELLANTS;
ANALYTICAL CHEMISTRY OF DIPHENYLAMINE IN PROPELLANTS
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JULIUS B. APATOFF
GEORGE NORWITZ

Project - Materials Testing Technology

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US Army Materials Testing Technology Program, which
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ment (in mechanical, chemical, or nondestructive
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Philadelphia, PA 19137

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I. SUMMARY

A comprehensive survey was made of the use of diphenylamine as a stabilizer in propellants. Various schemes that have been proposed for the degradation of diphenylamine in propellants to about 17 nitration products are described in detail. The effectiveness of the different degradation products to continue to act as stabilizers is discussed. The methods of analysis that have been proposed for the determination of diphenylamine and its degradation products in propellants and the status of the military requirements for such determinations are discussed.

II. RECOMMENDATIONS

The material in this report does not lend itself to incorporation into a specification or a standard. However, it is believed that the information will lead to clearer understanding of the complex mechanism of the stabilization of propellants by diphenylamine. Also, the information may lead to future programs for the establishment of better methods for the analysis for diphenylamine and its degradation products in propellants.

III. INTRODUCTION

Nitrocellulose-base propellants are essentially unstable materials that decompose on aging with the evolution of oxides of nitrogen. The decomposition is autocatalytic and can lead to failure of the ammunition or disastrous explosions. Many substances have been used to stabilize nitrocellulose-base propellants, but by far the most widely used substance is diphenylamine (DPA).

The purpose of the present report is to make a literature survey of the following: (a) the role of diphenylamine as a stabilizer in propellants; (b) the analytical chemistry of diphenylamine in propellants.
IV. STUDY

A. ROLE OF DIPHENYLAMINE AS A STABILIZER IN PROPELLANTS

The use of diphenylamine to suppress the autocatalytic decomposition of nitrocellulose contained in propellants was apparently first proposed by Nobel in a German patent in 1889 (48). Shortly afterwards, Germany in great secrecy adopted the use of diphenylamine for most propellants. However, other countries soon were using diphenylamine for this purpose and by about 1910 its use was fairly universal.

Berger in 1912 (5) was one of the first investigators to make a detailed study of the stabilization of propellants by DPA. He conducted experiments with the following propellants: a series containing DPA as a stabilizer, a series containing amyl alcohol as a stabilizer, and a series containing no stabilizer. He stored the propellants at temperatures up to 70°C and then tested them by a 110°C heat stability test. He found that the propellants containing DPA were much superior in stability to the other propellants. He also determined the nitrogen content of the nitrocellulose before and after the storage and found that it decreased less for the DPA-stabilized propellants than the other propellants.

Ryan and Ryan (57) in experiments to elucidate the nitration of diphenylamine studied the reaction of low concentrations of nitric acid and nitrous acid on diphenylamine and N-nitroso-diphenylamine dissolved in acetic acid. They isolated various nitrated diphenylamines.*

The same investigators (58) also made a study of the reactions of low concentrations of nitric and nitrous acid on diphenylamine and N-nitroso-diphenylamine dissolved in carbon tetrachloride.

Davis and Ashdown (8) developed color tests for the nitrated derivatives of diphenylamine, using alcoholic NaOH, alcoholic NH₃, alcoholic NaCN, and concentrated H₂SO₄. These tests are summarized in Table I.

* It is to be noted that earlier investigators did not in all cases use the presently recommended nomenclature for diphenylamine derivatives. For example, diphenylnitrosamine is now preferably called N-nitroso-diphenylamine, while p-nitro-diphenylamine is now preferably called 4-nitro-diphenylamine.
### Table I. Color Tests for Diphenylamine Derivatives (8)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Alcoholic NaOH</th>
<th>Alcoholic NH₃</th>
<th>Alcoholic NaCN</th>
<th>Conc. H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Nitro-DPA.................</td>
<td>Y</td>
<td>Y-GY</td>
<td>Y-GY</td>
<td>none</td>
</tr>
<tr>
<td>4-Nitro-DPA..................</td>
<td>YO-OY</td>
<td>GY</td>
<td>GY</td>
<td>RV</td>
</tr>
<tr>
<td>2,4'-Dinitro-DPA.............</td>
<td>OR</td>
<td>none</td>
<td>YO</td>
<td>YO-OY</td>
</tr>
<tr>
<td>2,4'-Dinitro-DPA.............</td>
<td>R-OR</td>
<td>Y-GY</td>
<td>OY</td>
<td>YO</td>
</tr>
<tr>
<td>4,4'-Dinitro-DPA.............</td>
<td>VR</td>
<td>GY</td>
<td>YG</td>
<td>RO</td>
</tr>
<tr>
<td>2,4,6-Trinitro-DPA..........</td>
<td>O-YO</td>
<td>O-YO</td>
<td>VR</td>
<td>0</td>
</tr>
<tr>
<td>2,4,4'-Trinitro-DPA..........</td>
<td>OR</td>
<td>O</td>
<td>OR</td>
<td>OR</td>
</tr>
<tr>
<td>2,4,6,4'-Tetranitro-DPA.....</td>
<td>YO</td>
<td>O-YO</td>
<td>B</td>
<td>OY</td>
</tr>
<tr>
<td>2,4,2',4'-Tetranitro-DPA....</td>
<td>RO</td>
<td>RO</td>
<td>OR-RO</td>
<td>OY</td>
</tr>
<tr>
<td>N-Nitroso-DPA................</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>B</td>
</tr>
</tbody>
</table>

Y = yellow, G = green, O = orange, R = red, B = brown, V = violet

Davis and Ashdown (8) found that diphenylamine in propellants was first converted into N-nitroso-diphenylamine. They concluded that this compound then rearranged under the influence of the acid products of decomposition, was oxidized and nitrated, and yielded 2,4' and 4,4'-dinitro-diphenylamine. These were finally nitrated to 2,4,4'-trinitro-diphenylamine. This scheme is shown in Figure 1. Davis and Ashdown believed that the last compound represented the final stage in the nitration of diphenylamine in propellants. They found that the examination of the nitrated derivatives in propellants furnished valuable information on the condition and past history of a propellant.
Hale (26) discussed the general stabilizing action of diphenylamine in propellants. He noted that nitrocellulose and propellants decomposed to NO which on contact with air formed NO₂ with the evolution of heat. When confined in contact with propellant both of these oxides of nitrogen, especially NO₂, promoted the decomposition of the propellant. Visual examination of an old unstable propellant usually revealed roughened discolored surfaces at ends and edges of the grains. Moisture markedly diminished the stability of propellants.

Marqueyrol (34) in a study of different stabilizers for smokeless powder heated samples containing up to 10% diphenylamine in open and closed containers at 40°C, 60°C, 75°C, 100°C, and 110°C for periods up to 4,083 days. The nitrogen content of the nitrocellulose was determined at intervals by nitrometer. His results showed that diphenylamine deteriorated markedly in propellants stored at 60°C and 75°C but only slightly at 40°C. N-nitroso-diphenylamine, which itself acted as a stabilizer, was produced. In addition, strongly colored secondary reaction products were formed. It was claimed that powder stabilized with N-nitroso-diphenylamine was superior to powder containing the same amount of diphenylamine. It was also found that N-nitroso-diphenylamine fixed the denitrated products of nitrocellulose in a stable form and, in contrast to diphenylamine, remained intimately mixed with the nitrocellulose because of its gelatinizing action on nitrocellulose. In experiments at 110°C it was found that the stabilizing properties of N-nitroso-diphenylamine were limited because this compound was partially destroyed at that temperature.
Muraour (43) stated that diphenylamine acted as a reducing agent on nitric esters and that copper salts catalyzed this reaction. Chlorides of the alkalies and alkali earths reinforced the effect of the copper salts, but organic salts such as oxalates and tartrates retarded the action.

Demougin and Landon (13) investigated the action of diphenylamine on nitrocellulose by determining loss in weight, change in nitrogen content, change in viscosity and Taliani results on powders containing up to 7.8% diphenylamine. These investigators found that too much diphenylamine (more than about 2.5%) was detrimental because of attack of the nitrocellulose. They ascertained this by heating samples of different diphenylamine content at 100°C for 160 hours and determining the change in nitrogen content. The results obtained are shown in Table II.

Table II. Relationship between the DPA Content of Smokeless Powder and Change in Nitrogen Content of Nitrocellulose (13)

<table>
<thead>
<tr>
<th>DPA Content (%)</th>
<th>In Fresh Powder</th>
<th>After Heating at 100°C for 160 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.02</td>
<td>12.82</td>
<td>11.89</td>
</tr>
<tr>
<td>2.20</td>
<td>12.89</td>
<td>13.01</td>
</tr>
<tr>
<td>3.75</td>
<td>12.76</td>
<td>11.14</td>
</tr>
<tr>
<td>7.80</td>
<td>12.58</td>
<td>10.13</td>
</tr>
</tbody>
</table>

Demougin and Landon (13) also concluded that the amount of stabilizer to be used should depend upon whether the powder is to be used immediately, stored at normal temperature, or stored at elevated temperatures.

Becker and Hunold (4) prepared pure nitro and nitroso products of the stabilizer in order to study their properties and their stabilizing action on nitrocellulose. They mixed the pure forms of these derivatives of diphenylamine with nitrocellulose, heated the mixture at 100°C, and noted the time which elapsed before the appearance of nitrogen gases. The results are summarized in Figure 2.
Figure 2. Time Elapsing Before Appearance of Nitrous Gases on Heating Mixtures of Diphenylamine Derivatives and Nitrocellulose at 100°C (4).
Becker and Kunold (4) also stated that in the presence of moisture the decomposition of nitrocellulose results in formation of nitrous and nitric acids. Nitrous acid changes the amine into nitrosamine, a process which often proceeds very rapidly and to some degree sets in during preparation of the powder. Under the influence of nitric acid, the nitroso group adheres to the amino nitrogen in the para position on the residual phenyl and is then simultaneously oxidized to the nitro group. As a result, 4-nitro-DPA is derived from N-nitroso-DPA.

In the same manner Becker and Hunold (4) found that 4,4- and 2,4-dinitro-DPA were formed from the mono-nitro-DPA’s. With the entrance of the NO group into dinitro-DPA, the basicity of the amine is so greatly reduced that the stabilizing action is materially lessened.

Becker and Hunold (4) also studied the transformation of diphenylamine in powders stored at 100°C with the aid of characteristic color reactions. They found that the nitroso compounds were present even in the unstored powder, but reached their maximum at the end of the first day. Tests showed that they were present throughout the storage period. The nitroso compounds were detected by means of the alpha-naphthylamine reaction. At the end of 24 hours mono-nitro-DPA was detected using the reaction with 10% alcoholic KOH. At the end of the second day the N-nitroso DPA showed a marked decrease, while a positive test was obtained for mono-nitro-diphenylnitrosamine and dinitro-DPA. At the end of the third day there was an increase of dinitro-DPA and the appearance of dinitro-diphenylnitrosamine. The latter increased in the next 24 hours and there was also evidence of trinitro-DPA. At the end of five days there was a decrease in dinitro-diphenylnitrosamine, while trinitro-DPA increased. By the end of the sixth day there was only a trace of the nitrosamines while trinitro-DPA still gave a strongly positive reaction with saturated alcoholic potassium cyanide solution.

The formation of the derivatives of diphenylamine on heating a powder at 100°C as summarized by Becker and Hunold (4) is shown in Figure 3.
Becker and Hunold (4) in view of their experimental work believed that diphenylamine in propellants was transformed in accordance with the scheme shown in Figure 4.
A report of the National Defense Research Committee, Division 8 (44)*, described methods for the chromatographic separation, identification, and quantitative estimation of several of the constituents of double-base powders. The constituents studied included diphenylamine, ethyl centralite and methyl centralite. In a subsequent report (45) the use of chromatographic methods was extended to the separation and quantitative determination of a number of powder constituents including diphenylamine, nitroso-diphenylamine, nitro-diphenylamine, nitro-diphenyl-dinitrosamine, dinitro-diphenylamine, dinitro-diphenyl-dinitrosamine, and trinitro-diphenylamine.

* National Defense Research Committee Reports are now no longer readily available.
an extensive study of diphenylamine and its derivatives. Spectro-
photometric data for these substances were obtained. Investigations
of the products of transformation of diphenylamine and the mechanism
of the stabilization of smokeless powder by this compound were carried
out on a series of samples of Ballistite JP 204 (a double-base
propellant) which had been heated at 160°F for lengths of time varying
from 1 day to 60 days. The compounds were first identified by their
chromatographic properties and streak tests. Identification was con-
firmed by spectrophotometric measurements. The following derivatives
of diphenylamine were detected: N-nitroso; 2-nitro; N-nitroso-4-nitro;
4-nitro; N-nitroso-2-nitro; 2,4-dinitro; 2,4'-dinitro; 2,2'-dinitro;
4,4'-dinitro; 2,2',4,4'-tetranitro; N-nitroso-4, 4'-dinitro; N-nitroso-
2,4'-dinitro; 2,4,4'-trinitro; 2,2',4-trinitro.

The results obtained (44) for a study of length of time during
which DPA and DPA derivatives are found in Ballistite JP 204 propellant
heated at 160°F are shown in Figure 5. Also included is data as to
whether more than 0.15 mg of the derivative was present per gram of
powder.
Figure 5. Approximate Period of Length of Time during Which Derivatives of DPA are Found in Ballistite JP 204 on Heating at 160°F (44).

--- more than 0.15 mg derivative present per gram of powder.

----- less than 0.15 mg derivative present per gram of powder.

Days of Heating
In another report of the National Defense Research Committee, Division 8 (46), methods were devised for the separation of about 20 nitro and nitroso derivatives of diphenylamine. With the exception of the N-nitroso compounds which were very labile, the derivatives of diphenylamine were determined roughly quantitatively with an accuracy probably better than 10%. This was accomplished by chromatographic isolation and spectrophotometric determinations. The following derivatives of diphenylamine were identified in this manner in aged propellant stored at elevated temperatures:

<table>
<thead>
<tr>
<th>DPA</th>
<th>4,4'-dinitro-DPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-nitroso-DPA</td>
<td>N-nitroso-2,4'-dinitro-DPA</td>
</tr>
<tr>
<td>2-nitro-DPA</td>
<td>N-nitroso-4,4'-dinitro-DPA</td>
</tr>
<tr>
<td>4-nitro-DPA</td>
<td>2,2',4-trinitro-DPA</td>
</tr>
<tr>
<td>N-nitroso-2-nitro-DPA</td>
<td>2,4,4'-trinitro-DPA</td>
</tr>
<tr>
<td>N-nitroso-4-nitro-DPA</td>
<td>2,2',4,4',6-tetranitro-DPA</td>
</tr>
<tr>
<td>2,2'-dinitro-DPA</td>
<td>2,2',4,4',6-pentanitro-DPA</td>
</tr>
<tr>
<td>2,4'-dinitro-DPA</td>
<td>2,2',4,4',6,6'-hexanitro-DPA</td>
</tr>
<tr>
<td>2,4-dinitro-DPA</td>
<td>picric acid</td>
</tr>
</tbody>
</table>

The above investigators reported the time periods observed for the appearance, formation of maximum quantity, and exhaustion of the diphenylamine derivatives on heating Ballistite JP 204 at 71°C. These results are shown in Table III.

Table III. Approximate Time of Appearance, Maximum Quantity, and Exhaustion of the Derivatives of DPA in JP 204 Powder Heated at 71°C (46).

<table>
<thead>
<tr>
<th>Approximate Time in Days of</th>
<th>DPA</th>
<th>Appearance</th>
<th>Maximum Quantity</th>
<th>Exhaustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-nitroso-DPA</td>
<td>0</td>
<td>5</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>2-nitro-DPA</td>
<td>0</td>
<td>10</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>4-nitro-DPA</td>
<td>0</td>
<td>20</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>N-nitroso-4-nitro-DPA</td>
<td>5</td>
<td>20</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>2,2'-dinitro-DPA</td>
<td>5</td>
<td>40</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>2,4'-dinitro-DPA</td>
<td>5</td>
<td>30</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>4,4'-dinitro-DPA</td>
<td>5</td>
<td>30</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>2,2',4-trinitro-DPA</td>
<td>5</td>
<td>95</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>2,4,4'-trinitro-DPA</td>
<td>8</td>
<td>60</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Tetranitro-DPA</td>
<td>25</td>
<td>125</td>
<td>&gt; 260</td>
<td></td>
</tr>
<tr>
<td>Pentanitro-DPA</td>
<td>125</td>
<td>?</td>
<td>&gt; 260</td>
<td></td>
</tr>
<tr>
<td>Hexanitro-DPA</td>
<td>~125</td>
<td>?</td>
<td>&gt; 260</td>
<td></td>
</tr>
<tr>
<td>Picric Acid</td>
<td>~150</td>
<td>?</td>
<td>&gt; 260</td>
<td></td>
</tr>
</tbody>
</table>
The same authors (46) stated that diphenylamine and its derivatives, in addition to being converted into substances which were not recovered immediately, appeared to be principally nitrated and N-nitrosated (and denitrosated) in a series of competing and consecutive reactions. These reactions resulted in the accumulation of nitro and nitroso groups at a constant rate while diphenylamine was present and thereafter at a much lower rate which remained nearly constant for a long time. With the exception of the reactions yielding nitroso-DPA and 2,2',4,4'-tetranitro-DPA, the successive reactions occurred with increasing difficulty. This was a reasonable consequence of substituting deactivating groups onto the diphenylamine nucleus. Both N-nitroso-DPA and tetranitro-DPA, however, appeared less reactive than their immediate postcursors as well as being less reactive than their immediate precursors. They accordingly accumulated to a greater extent and tended to persist relatively longer than do any of the other members of the series.

The same authors (46) believed that not all of the active substances liberated in the decomposition of the organic nitrates actually react with diphenylamine and its derivatives. They asserted that an unknown proportion reacts with the remainder of the powder, causing the decomposition of the organic nitrates to accelerate to an unknown degree. This was just sufficient to maintain the observed total rate of conversion of the diphenylamine derivatives. Their data indicated convincingly that both N-nitrosation and denitrosation occur but that the distinction between these mechanisms was not feasible. They concluded that diphenylamine is first nitrosated and then converted into 2-nitro-DPA, 4-nitro-DPA, N-nitroso-4-nitro-DPA, etc., and that diphenylamine is not directly nitrated to 2-nitro-DPA or 4-nitro-DPA. However, it is by no means certain that direct nitration of diphenylamine does not also play a role during the first 5 days of heating, nor that denitrosation of N-nitroso-DPA does not occur to a significant extent. It was suggested that 2-nitro-DPA, 4-nitro-DPA and even 4,4'-dinitro-DPA are better stabilizers at 71°C than N-nitroso-DPA, N-nitroso-4-nitro-DPA, or 2,4,4'-trinitro-DPA or for that matter, diphenylamine itself.

In another report, the National Defense Research Committee, Division 8 (47), found the same nitro and nitroso derivatives were formed in FNH and single-base powder as were encountered in double-base powder. However, they found the overall rate of transformation in single-base powder was only about one-tenth that in double-base powder and was even slightly slower in FNH powder. The results obtained in a study of the effect of heating single-base propellants at 65.5°C for up to 400 days are shown in Table IV. The samples consisted of a mixture of light and dark grains as in the original powder. Results are expressed in mg of each compound isolated from 1 gram of powder.
Table IV. Nitro and Nitroso Derivatives Isolated from Single-Base Powder Heated at 65.5°C (47)

<table>
<thead>
<tr>
<th>Days of Heating</th>
<th>Control</th>
<th>7</th>
<th>15</th>
<th>28</th>
<th>62</th>
<th>92</th>
<th>122</th>
<th>183</th>
<th>304</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light</td>
<td>Dark</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPA (mg)</td>
<td>4.32</td>
<td>3.18</td>
<td>3.90</td>
<td>3.14</td>
<td>2.27</td>
<td>1.15</td>
<td>0.27</td>
<td>0.01</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>N-nitroso-DPA (mg)</td>
<td>0.30</td>
<td>0.59</td>
<td>0.74</td>
<td>1.20</td>
<td>1.56</td>
<td>2.63</td>
<td>3.30</td>
<td>2.37</td>
<td>1.43</td>
<td>0.23</td>
</tr>
<tr>
<td>2-nitro-DPA (mg)</td>
<td>----</td>
<td>0.06</td>
<td>0.12</td>
<td>0.16</td>
<td>0.19</td>
<td>0.21</td>
<td>0.21</td>
<td>0.35</td>
<td>0.38</td>
<td>0.06</td>
</tr>
<tr>
<td>4-nitro-DPA (mg)</td>
<td>----</td>
<td>0.05</td>
<td>0.11</td>
<td>0.20</td>
<td>0.22</td>
<td>0.35</td>
<td>0.41</td>
<td>0.46</td>
<td>0.28</td>
<td>0.05</td>
</tr>
<tr>
<td>N-nitroso-4-nitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>0.003</td>
<td>0.003</td>
<td>0.008</td>
<td>----</td>
<td>----</td>
<td>0.32</td>
<td>0.87</td>
<td>0.29</td>
</tr>
<tr>
<td>2,4'-dinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>0.007</td>
<td>0.004</td>
<td>0.016</td>
<td>0.007</td>
<td>0.007</td>
<td>0.054</td>
<td>0.52</td>
<td>1.43</td>
</tr>
<tr>
<td>4,4'-dinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>0.003</td>
<td>0.001</td>
<td>0.002</td>
<td>0.003</td>
<td>0.009</td>
<td>0.096</td>
<td>0.73</td>
<td>1.21</td>
</tr>
<tr>
<td>2,2'-dinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.04</td>
<td>0.10</td>
</tr>
<tr>
<td>2,4-dinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>2,4,4'-trinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.009</td>
<td>0.051</td>
</tr>
<tr>
<td>2,2',4-trinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>DPA accounted for (mg)</td>
<td>4.56</td>
<td>3.77</td>
<td>4.80</td>
<td>4.46</td>
<td>3.80</td>
<td>3.84</td>
<td>3.59</td>
<td>2.99</td>
<td>3.24</td>
<td>2.97</td>
</tr>
</tbody>
</table>
A sample of single-base powder which had been stored under normal magazine conditions for 37 years retained 36% of its original diphenylamine either as DPA or its nitroso and nitro derivatives (47). About 20% of the original diphenylamine was accounted for as available diphenylamine. The results of determinations made on ten samples of single-base powder which had been heated at 65.5°C for from 0 to 365 days are plotted in Figure 6. The decrease in diphenylamine is apparently linear. Both the increase and decrease in N-nitroso-diphenylamine occurred, however, with a decreasing rate. The quantity of 2-nitro-DPA present in the powder exceeded that of its 4-nitro isomer at all times. At the end of the heating period (365 days) the dinitro-DPA's appeared to accumulate.

The decrease of the stabilizer was not uniform in all powders; it was linear in both FNH and double-base powder but followed a decreasing rate in single-base pyro powder. N-nitroso-DPA increased linearly in both single and double base powder but proceeded with a decreasing rate in FNH powders. The decrease of the N-nitroso compound occurred, however, with a decreasing rate in all three powders. The increase and decrease of 2-nitro-DPA with respect to that of 4-nitro-DPA did not follow identical patterns in the two types of powders.

After the depletion of diphenylamine, the percentage of diphenylamine which is accounted for as its derivatives fell to a nearly constant level of 60 to 65%, in single as well as in double-base powders.

In summary (47), the following possible reactions were proposed as being responsible for the conversion of one derivative into another: (a) N-nitrosation, (b) denitrosation, (c) direct nitration of amines, (d) direct nitration of nitrosamines followed or accompanied by denitrosation (or followed by further nitration), (e) rearrangement of nitrosamines (as in Fischer-Hepp reaction) followed by oxidation, and (f) oxidation of nitrosamines to nitroamines followed by rearrangement.
Figure 6. Decrease of DPA and Increase of DPA Derivatives in FNH Powder Heated at 65.5°C (47).
Schroeder et al (59) made quantitative estimations of diphenylamine derivative powders, by means of a chromatographic-spectrophotometric technique. They concluded that following initial formation of N-nitroso-DPA, further reactions of this compound probably involves direct nitration to 4-nitroso-4-nitro-DPA rather than rearrangement and oxidation. Also, the role of the rearrangement probably decreases as the compounds become more highly nitrated. The formation of tri-nitro-diphenylamines and more highly nitrated compounds, involves direct introduction of the nitro group into the molecule.

The derivatives of diphenylamine isolated by Schroeder et al (59) from grains of Ballistite JP-204 after storage at 71°C are shown in Table V. The results are expressed in mg of each compound isolated from 1 gram of powder.

Gizycki (24) studied the slow decomposition of nitrocellulose at 100°C by measuring weight loss, change in viscosity, and nitrogen content. He found that weight loss and change in nitrogen content were markedly retarded by diphenylamine. The decrease in viscosity, however, was not inhibited.
Table V. Nitro and Nitroso Derivatives Isolated From Ballistite JP-204 Powder Heated at 71°C (59)

<table>
<thead>
<tr>
<th>Days of Heating</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>20</th>
<th>35</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPA (mg)</td>
<td>7.11</td>
<td>4.27</td>
<td>1.60</td>
<td>0.0</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>N-nitroso-DPA (mg)</td>
<td>0.42</td>
<td>2.08</td>
<td>3.55</td>
<td>4.47</td>
<td>2.35</td>
<td>0.78</td>
<td>0.18</td>
</tr>
<tr>
<td>2-nitro-DPA (mg)</td>
<td>0.08</td>
<td>0.13</td>
<td>0.10</td>
<td>0.31</td>
<td>0.24</td>
<td>0.09</td>
<td>----</td>
</tr>
<tr>
<td>4-nitro-DPA (mg)</td>
<td>0.02</td>
<td>0.07</td>
<td>0.09</td>
<td>0.14</td>
<td>0.35</td>
<td>0.18</td>
<td>0.04</td>
</tr>
<tr>
<td>N-nitroso-4-nitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.45</td>
<td>0.96</td>
<td>0.21</td>
<td>----</td>
</tr>
<tr>
<td>2,2'-dinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.04</td>
<td>0.29</td>
<td>0.45</td>
<td>0.42</td>
</tr>
<tr>
<td>2,4'-dinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.19</td>
<td>1.01</td>
<td>1.51</td>
<td>0.95</td>
</tr>
<tr>
<td>4,4'-dinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.06</td>
<td>0.56</td>
<td>0.83</td>
<td>0.47</td>
</tr>
<tr>
<td>2,2',4-trinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.02</td>
<td>0.16</td>
<td>0.67</td>
<td>1.36</td>
</tr>
<tr>
<td>2,4,4'-trinitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.01</td>
<td>0.34</td>
<td>1.57</td>
<td>3.21</td>
</tr>
<tr>
<td>Tetra-nitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.07</td>
<td>0.23</td>
</tr>
<tr>
<td>Penta-nitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Hexa-nitro-DPA (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Picric Acid (mg)</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>DPA equiv. (mg)</td>
<td>7.55</td>
<td>6.24</td>
<td>4.79</td>
<td>4.68</td>
<td>4.65</td>
<td>4.12</td>
<td>4.03</td>
</tr>
<tr>
<td>Percent</td>
<td>100</td>
<td>83</td>
<td>64</td>
<td>62</td>
<td>62</td>
<td>55</td>
<td>53</td>
</tr>
</tbody>
</table>

Where no value is given the quantity is less than 0.01 mg.
Table V. Nitro and Nitroso Derivatives Isolated From Ballistite JP-204 Powder Heated at 71°C (59) (cont’d)

<table>
<thead>
<tr>
<th>Days of Heating</th>
<th>82</th>
<th>124</th>
<th>174</th>
<th>258</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yellow</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>DPA (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-nitroso-DPA (mg)</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-nitro-DPA (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-nitro-DPA (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-nitroso-4-nitro-DPA (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2'-dinitro-DPA (mg)</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4'-dinitro-DPA (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4'-dinitro-DPA (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2',4-trinitro-DPA (mg)</td>
<td>2.08</td>
<td>1.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4,4'-trinitro-DPA (mg)</td>
<td>2.18</td>
<td>0.01</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Tetrinitro-DPA (mg)</td>
<td>3.51</td>
<td>7.52</td>
<td>2.75</td>
<td>0.57</td>
</tr>
<tr>
<td>Pentanitro-DPA (mg)</td>
<td></td>
<td>0.09</td>
<td>2.40</td>
<td>0.75</td>
</tr>
<tr>
<td>Hexanitro-DPA (mg)</td>
<td></td>
<td></td>
<td>4.75</td>
<td>6.25</td>
</tr>
<tr>
<td>Picric Acid (mg)</td>
<td></td>
<td></td>
<td>0.16</td>
<td>0.0</td>
</tr>
<tr>
<td>DPA equiv. (mg)</td>
<td>4.10</td>
<td>4.70</td>
<td>4.37</td>
<td>3.01</td>
</tr>
<tr>
<td>Percent</td>
<td>54</td>
<td>62</td>
<td>58</td>
<td>40</td>
</tr>
</tbody>
</table>

Where no value is given the quantity is less than 0.01 mg.
Levitsky (32) stored three types of propellants at elevated and ambient temperatures for 56 weeks. All three types exhibited some degree of ballistic instability with storage at elevated temperatures. The infrared, ultraviolet, and visible spectra of the methylene chloride extracts of these propellants were determined. The spectra of the samples stored at elevated temperatures were compared with those stored at ambient temperatures. Changes in chemical composition of all three types of propellants were indicated, the major changes being attributed to a depletion of the diphenylamine.

Quinlan (53) stated that degradation of nitrocellulose (13.85% N) on exposure to gaseous nitrogen dioxide in a dry atmosphere at room temperature was slow. However, upon addition of a little water vapor the time required to reach the same degree of denitration (9 to 10% N) was 48 hours as compared to 192 hours under anhydrous conditions. Similar results were obtained with propellant samples. It was stated that a trace of acid is necessary to initiate decomposition of nitrocellulose by nitrogen oxides. This trace of acid may originate from insufficient washing of the nitrocellulose or from a minute quantity of an unstable nitric ester or sulfonitric ester. Quinlan concluded that an increase in the nitrogen content of nitrocellulose is accompanied by a corresponding increase in the tendency toward decomposition, with a relationship that is exponential rather than linear. Also, Quinlan concluded that the chemical stability of solid propellants varies inversely as the nitroglycerin content.

DeAngelis and Cardin (9) stated that the decomposition of stabilized propellants appear to be a two-step pseudo first-order reaction in stabilizers with the second step rate-determining. Stabilized propellants can be regarded as a two-component system consisting of nitrocellulose and stabilizer, while the other ingredients in the formulation can be considered inert or catalysts, either promotors or poisoners. Chemical kinetics were used to develop the mechanism of reaction which was substantiated by experimental proof.

Yasuda (62) made up a comparative study of stabilizer capacity towards nitrogen dioxide by means of a gasometric liberation procedure. In terms of weight of N₂O₄ reacted per unit weight of stabilizer, the following order of effectiveness was obtained: diphenylamine >N,N'-diphenylbenzidine=N,N'-diethyl-N,N'-diphenylurea >2-nitrodiphenylamine >2-diphenylurea=2,4-dinitrodiphenylamine.

Lazarveric (31) made a study of the effectiveness of different stabilizers and powders with a high nitroglycerin. He concluded that the centralites were more effective stabilizers for this purpose than diphenylamine. He found that the stability of the propellant (as indicated by various heat tests) decreased with increasing nitroglycerin content. He also noted that the stability decreased somewhat with increasing nitrogen content of nitrocellulose. He observed that the
reaction of the nitrogen oxides with the stabilizer was more effective with powder grains of thicker walls than thinner walls because on heating layer grain powder, nitrogen oxides must pass a longer distance through the grain before they are liberated.

Apatoff and Cohen (3) stored seven lots of propellant at Frankford Arsenal for 80 weeks at 140°F and at intervals determined available stabilizer, actual diphenylamine, primary degradation products, and the nitrogen content of the nitrocellulose. Initial and final results of the analyses in this previously unpublished study are given in Table VI. The available stabilizer markedly decreased by the end of the test with a similar decrease in the actual diphenylamine. N-nitroso-diphenylamine was present in fairly large amounts in double-base propellants at the end of the test but had decreased considerably in single-base propellants. The amount of 2-nitrodiphenylamine increased in the double-base propellants but did not change significantly in the single-base propellants. The total as diphenylamine showed a marked drop at the end of the test, especially in the single-base propellants. The nitrogen content of the nitrocellulose showed a marked decrease in the double-base propellants and only a moderate decrease in the single-base propellants.

Modern theories of electron displacement as elucidated by Pauling (51) and Ingold (28) may be used to explain the reaction patterns of diphenylamine. Laccetti and Roth (29) examined this aspect in detail.
Table VI. Study of the Effect of Heating  
Single-Base and Double-Base  
Propellants for 80 Weeks at  
140°F (3)

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Aa</th>
<th>Ba</th>
<th>Ca</th>
<th>Da</th>
<th>Ea</th>
<th>Pb</th>
<th>Cb</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Available Stabilizer (DPA)</strong>&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of Test</td>
<td>0.83</td>
<td>0.85</td>
<td>0.72</td>
<td>0.73</td>
<td>0.84</td>
<td>0.63</td>
<td>0.69</td>
</tr>
<tr>
<td>End of Test</td>
<td>0.13</td>
<td>0.30</td>
<td>0.31</td>
<td>0.38</td>
<td>0.14</td>
<td>0.01</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>Actual DPA&lt;sup&gt;d&lt;/sup&gt;</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of Test</td>
<td>0.76</td>
<td>0.73</td>
<td>0.70</td>
<td>0.69</td>
<td>0.72</td>
<td>0.79</td>
<td>0.69</td>
</tr>
<tr>
<td>End of Test</td>
<td>0.0</td>
<td>0.14</td>
<td>0.11</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>N-nitroso-DPA&lt;sup&gt;d&lt;/sup&gt;</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of Test</td>
<td>0.11</td>
<td>0.15</td>
<td>0.17</td>
<td>0.32</td>
<td>0.25</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>End of Test</td>
<td>0.35</td>
<td>0.45</td>
<td>0.48</td>
<td>0.56</td>
<td>0.30</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>2-nitro-DPA&lt;sup&gt;d&lt;/sup&gt;</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of Test</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
<td>0.06</td>
<td>0.18</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>End of Test</td>
<td>0.13</td>
<td>0.14</td>
<td>0.14</td>
<td>0.09</td>
<td>0.14</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td><strong>Total as DPA&lt;sup&gt;d&lt;/sup&gt;</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of Test</td>
<td>0.92</td>
<td>0.90</td>
<td>0.88</td>
<td>1.00</td>
<td>1.07</td>
<td>0.87</td>
<td>0.94</td>
</tr>
<tr>
<td>End of Test</td>
<td>0.39</td>
<td>0.63</td>
<td>0.63</td>
<td>0.58</td>
<td>0.17</td>
<td>0.11</td>
<td>0.17</td>
</tr>
<tr>
<td><strong>% N in Nitrocellulose</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>End of Test</td>
<td>9.55</td>
<td>8.66</td>
<td>12.63</td>
<td>9.43</td>
<td>7.66</td>
<td>12.55</td>
<td>12.82</td>
</tr>
</tbody>
</table>

<sup>a</sup> Double-base propellant (WC-846 Type).  
<sup>b</sup> Single-base propellant (IMR Type).  
<sup>c</sup> Determined as described in MIL-STD-286B (42).  
<sup>d</sup> Determined as described in Picatinny Arsenal Report 58-HI-648 (30).
The melting points for the derivatives of diphenylamine and discussion of methods of preparation are given by Ryan and Glover (55), Davis and Ashdown (8), and Schroeder et al (59).

B. ANALYTICAL CHEMISTRY OF DIPHENYLAMINE IN PROPELLANTS

Ryan, Keane, and Dunne (56) determined diphenylamine in propellants by extracting with alcohol, treating the extract with stannous chloride and hydrochloric acid, and steam distilling the diphenylamine. They then extracted the diphenylamine from the distillate with chloroform and determined it by volumetric bromination with bromine dissolved in chloroform. They found that the consumption of bromine was greater than theoretical when mixtures of two nitro derivatives of diphenylamine were present, especially when one of the derivatives was diphenylamine.

Cook (6) described the following four methods for the determination of diphenylamine in propellants:

(a) The nitration method, which gives the total diphenylamine originally added. Cook proposed the use of a mixture of acetic and nitric acids for the nitration and a conversion factor of 0.4259. The method was applicable to newly manufactured propellants. In old or reworked powders it gave only the total diphenylamine added and failed to show the amount of available or active diphenylamine.

(b) The sodium hydroxide distillation method which, according to Cook gave only the active or available diphenylamine. In this method the propellant was distilled with steam in a 10% sodium hydroxide solution and the distillate extracted with ether. The ether extract was treated with bromine to produce tetrabromdiphenylamine, the ether was evaporated; and the residue boiled with 5% sodium hydroxide solution. The tetrabromdiphenylamine was then filtered through a Gooch, dried, and weighed.

(c) The extraction method which gave both the active and inactive diphenylamine. In this method the diphenylamine was extracted with ether in a Soxhlet apparatus and the extract steam distilled. The diphenylamine was then extracted with ether and brominated.

(d) The volumetric method which gave the active or available diphenylamine in new propellants. The extracted powder was brominated with a 0.2N potassium bromate-bromide solution, hydrochloric acid was
added, the flasks were allowed to stand for 2 minutes, and 10 ml of a 10% solution of KI was added. After 3 minutes the mixture was titrated with 0.1N sodium thiosulfate, using starch as an indicator. The author experienced difficulty getting an end point when the powder contained N-nitroso-diphenylamine.

Waugh, Harbottle, and Noyes (61) suggested glacial acetic acid instead of alcohol as a solvent in the volumetric bromination method.

Ellington (23) performed steam distillation of the propellant followed by volumetric bromination. He treated the distillate with titanous sulfate to remove interferences.

Norvall, Ovenston, and Parker (49) determined diphenylamine in propellants by extracting with 90% acetic acid, adding dilute sulfuric acid and potassium dichromate, and measuring the blue color. Grodzinski (25) used a somewhat similar approach but extracted with ethyl alcohol.

Apatoff and Cohen (1) evaluated wet methods for the determination of diphenylamine in ball propellants. They concluded that results obtained by the volumetric method (40) were, in general, lower than those by the gravimetric (41) and steam distillation methods (42). They found that the gravimetric procedure gave the highest results of the three methods. This was particularly true of propellants containing nitrated products of diphenylamine. Also, for samples containing nitrated products of diphenylamine, the steam distillation method using the gravimetric bromination method gave higher results than the volumetric method.

Marvillet and Tranchant (36) determined diphenylamine by dissolution of the propellant with acetic acid and acetic anhydride, cooling to 0°C, and titrating with 0.025N perchloric acid in acetic acid-acetic anhydride medium, using glass and silver-silver chloride electrodes. Centralite, 2-nitro-diphenylamine, N-nitroso-diphenylamine, nitrocellulose, dinitrotoluene and dibutylphthalate did not interfere. The same investigators (37, 38) proposed nonaqueous titration methods for the determination of 2-nitro- and 2,4-dinitro-diphenylamine using basic solvents such as dimethylformamide or pyridine and Bu₃MeNOH in isopropyl alcohol as the titrant. Also, they described methods for the determination of diphenylamine, N-nitroso-diphenylamine, and ethyl centralite in the presence of each other. These three compounds were extracted with methylene chloride and an aliquot of the extract was brominated and titrated iodometrically. The remainder of the extract was evaporated and the residue dissolved in acetic acid. Half of this solution was used for the determination of diphenylamine by titrating with perchloric acid after treatment with acetic anhydride. The other half of the solution was used for the determination of N-nitroso-diphenylamine by reacting with alpha-naphthylamine and titrating the excess alpha-naphthylamine. Centralite was estimated by difference.
Laccetti and Roth (29) described spectrophotometric procedures for the determination of actual diphenylamine and its primary degradation products (N-nitroso-diphenylamine and 2-nitro-diphenylamine). Laccetti, Younginer, and Roth (30) later improved on this procedure. This method will be discussed in detail later.

Roth (54) described a co-operative study of the spectrophotometric determination of available stabilizer in aged propellants, containing either diphenylamine or ethyl centralite. The study included standardization of spectrophotometric factors for diphenylamine and ethyl centralite. The diphenylamine was measured at 285 nm and the ethyl centralite at 247 nm.

The work of the National Defense Committee, Division 8 (44), and Schroeder et al (59) on the separation of the diphenylamine derivatives by column chromatography followed by ultraviolet determination has been previously mentioned.

Ovenston (50) stated that there are 24 ether-soluble ingredients in powders which can be separated and identified by column chromatography. For all except mineral jelly, a good adsorbent is a mixture of silica gel and Celite 535. The best developing solvent was petroleum ether (b.p. 40-50°C) mixed with benzene or ethyl ether. Streak tests were proposed for the identification of each ingredient.

Several investigators have used thin layer chromatography in the detection and determination of diphenylamine derivatives in propellants. Hansson and Alm (27) found benzene to be a better solvent than chloroform or toluene for chromatographing diphenylamine and its nitro derivatives on thin layers of silicic acid. Spots were made visible by treating with 0.2% alcoholic sodium nitrite and 1N H$_2$SO$_4$. $R_f$ values were tabulated for diphenylamine, N-nitroso-diphenylamine, 4-nitro-diphenylamine, 2-nitro-diphenylamine, 2,4-dinitro-diphenylamine, 2,4'-dinitro-diphenylamine, and sym. hexanitro-diphenylamine and triphenylamine with 3 solvents.

del Campo (11) using thin layer chromatography detected the following in certain U. S., French, Belgian, and Spanish propellants: diphenylamine, 2-nitro-diphenylamine, N-nitroso-diphenylamine, centralite, nitroglycerin, and other compounds. The stationary phase was silica gel 6. The unknown was extracted with methylene chloride and eluted with benzene. In subsequent investigations the same author (12) applied the technique to additional propellants. Visualization of diphenylamine and its derivatives and centralite was performed by spraying with Muraour's reagent (5 grams of potassium dichromate, 100 ml acetic acid, 50 ml sulfuric acid, and 100 ml water). Phthalates and nitroglycerin were made visible by treating with a solution of resorcinol in sulfuric acid. Trinitrotoluene, triacetin, and diphenylurethane were determined by using different spray reagents.
Yasuda (63) separated and identified the derivatives of diphenylamine by two dimensional thin layer chromatography on silica gel containing zinc dust. The following derivatives of diphenylamine were separated and identified with p-diethylaminobenzaldehyde: 2-nitro; N-nitroso; N-nitroso-4-nitro; 2,4-dinitro; 2,4,6'-trinitro; 2,4'-dinitro; 2,2'-dinitro; N-nitroso-4,4'-dinitro; N-nitroso-2-nitro; 4-nitro; N-nitroso,2,4'-dinitro; 2,4,4'-trinitro; 2,2',4-trinitro; N-nitroso-2,2'-dinitro; 4-nitroso; 2,2',4,4'-tetrinitro, 2,2',4,4',6-pentanitro; 4,4'-dinitro; 2,2',4,4', 6,6'-hexanitro.

Pristera (52) developed a qualitative infrared method for the analysis of common ether-soluble ingredients of propellants. Infrared spectra were given for diphenylamine, nitroso-diphenylamine, and 2-nitro-diphenylamine among other propellant ingredients. Quantitative infrared methods for analyzing mixtures of several ingredients were also discussed.

Levitsky, Norwitz, and Chasan (33) studied the infrared spectra of the various nitrated derivatives of diphenylamine.

Sourd (60) described a polarographic method for the determination of diphenylamine, dibutylphthalate, and dinitrotoluene in propellants.

Apatoff and Cohen (2) developed a method for the determination of diphenylamine and ethyl centralite in admixture. In this procedure the propellant containing both stabilizers was steam distilled and the distillate extracted with ether and made to a definite volume. Half of the solution was brominated gravimetrically, the brominated centralite going into solution. The insoluble brominated diphenylamine was collected on a crucible, weighed, and calculated to diphenylamine. The remainder of the ether extract was evaporated, the residue dissolved in glacial acetic acid, and the volumetric bromination procedure applied, thus obtaining a total thiosulfate titration for both stabilizers. The diphenylamine content was converted to its equivalent volume of thiosulfate solution and subtracted from the total. The remaining volume of thiosulfate solution was calculated to ethyl centralite.

DeAtley (10) described a spectrophotometric method for the determination of diphenylamine, 2-nitro-diphenylamine, or 4-nitro-diphenylamine by oxidation with Fe+++ in sulfuric acid solution in a boiling water bath after a preliminary methylene chloride extraction. 2,4-dinitro-diphenylamine, 2,4'-dinitro-diphenylamine, 2,4-dinitrotoluene, and centralites did not interfere. N-nitroso-diphenylamine produced the same color as diphenylamine.

The status of the determination of diphenylamine and its derivatives insofar as U. S. Military inspection requirements are concerned is as follows:
1. The method for Available Stabilizer (Diphenylamine and Ethyl Centralite) (17, 42) has been canceled. This method was intended for the determination of diphenylamine and ethyl centralite when present together in propellants or for determining the percent "available stabilizer" calculated as diphenylamine or ethyl centralite. This determination did not distinguish between them or their primary degradation products. Steam distillation of the propellant, however, has been shown to be a valuable procedure in determining available stabilizer.

2. The following methods are now presently recommended for the determination of diphenylamine and its derivatives in propellants:

(a) Distillation Procedure for Diphenylamine or Ethyl Centralite (Volumetric Bromination Method) (20). This method is suitable for determining the diphenylamine or ethyl centralite content in either aged or newly manufactured propellants. Other propellant ingredients that steam distill and are brominatable will interfere. This method may be used for determining the percentage of "available stabilizer" calculated as diphenylamine or ethyl centralite but does not distinguish between them and their primary degradation products. The propellant is steam distilled in dilute caustic solution thereby effecting a conversion of the primary degradation products to diphenylamine (30). The distillate is subjected to volumetric bromination and the "available stabilizer" calculated to diphenylamine or ethyl centralite.

(b) Volumetric Bromination Method (14, 18, 21). This method is used for determining the diphenylamine content of newly manufactured single-base or double-base propellants containing no other brominatable material (such as salicylates, phenols, or centralite). The propellant is extracted overnight with methylene chloride, the solvent is removed by aeration and the dry residue dissolved in glacial acetic acid. Diphenylamine is determined by volumetric bromination.

(c) Increase in Weight Method (16, 22a) which entails the bromination of the solvent extract of the propellant and weighing the tetrabromodiphenylamine precipitate. It is applicable only to newly manufactured propellants, and to samples containing no other brominatable material. The factor used to convert the brominated diphenylamine does not apply to derivatives of diphenylamine.

(d) Gravimetric Method (15, 22, 41) which again is applicable only to newly made propellants and to samples containing no other brominatable material. This method, like the increase in weight method, does not give the actual diphenylamine present.
(e) Diphenylamine and Ethyl Centralite in Admixture or Separately (Spectrophotometric Method) (20). This method is suitable for determining the diphenylamine and ethyl centralite contents in either aged or newly manufactured propellants. Other propellant ingredients that steam distill and absorb at the wave length used for analysis will interfere. The propellant is steam distilled from caustic solution and the distillate is diluted with ethyl alcohol. The absorbance is determined at 285 nm if only diphenylamine is present, at 247 nm if only ethyl centralite is present, or at both wavelengths if both diphenylamine and ethyl centralite are present.

(f) Gas Chromatographic Method (20a) for the determination of diphenylamine (and also dinitrotoluene, phthalates, ethylene dimethacrylate and other plasticizers and stabilizers) in single-base propellants after a methylene chloride extraction. A silicone rubber UC-W98 column is used at 200°C. The method is not applicable to double-base propellants because of decomposition of nitroglycerin in the column.

(g) Determination of Actual Diphenylamine, N-Nitroso-diphenylamine, and 2-Nitro-diphenylamine (30). This method determines the amount of actual or active diphenylamine and two of its primary degradation products, N-nitroso-diphenylamine, and 2-nitro-diphenylamine. The propellant is initially extracted with methylene chloride and two aliquots of the extract are evaporated to remove the solvent. One aliquot is steam distilled from a caustic solution, the distillate diluted with ethanol, and the absorbance is measured at 285 nm for diphenylamine and at 430 nm for 2-nitro-diphenylamine. Another aliquot is steam distilled from a water solution, the distillate diluted with ethanol, an aliquot is reacted with alpha-naphthylamine, and the N-nitroso-diphenylamine is measured at 550 nm. Since the measurement for diphenylamine will also include the amounts of 2-nitro and N-nitroso derivatives which have been converted back to diphenylamine during the distillation from the caustic solution, the amounts of these derivatives which have been determined independently are subtracted from the measured diphenylamine to obtain the actual or active diphenylamine.
V. BIBLIOGRAPHY


(15) Ibid., Method 201.2.3.

(16) Ibid., Method 201.3.3.

(17) Ibid., Method 217.2.1.

(19) Ibid., Method 201.4.1.
(20) Ibid., Method 217.3.
(20a) Ibid., Method T226.1.
(22) Ibid., Method 201.2.2.
(22a) Ibid., Method 201.3.2.
(23) Ellington, F., Analyst, 71, 305 (1946).
(26) Hale, G. C., Army Ordnance, 2, 674 (1925).


(41) Ibid., Method 201.2.

(42) Ibid., Method 217.2(T).

(43) Muraour, H., *Compt. rend.*, 197, 758 (1933).


(58) Ibid., 34B, 212 (1919).


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**11. SUPPLEMENTARY NOTES**

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**13. ABSTRACT**

A comprehensive survey was made of the use of diphenylamine as a stabilizer in propellants. Various schemes that have been proposed for the degradation of diphenylamine in propellants to about 17 nitration products are described in detail. The effectiveness of the different degradation products to continue to act as stabilizers is discussed. The methods of analysis that have been proposed for the determination of diphenylamine and its degradation products in propellants and the status of the military requirements for such determinations are discussed.
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<td>Nitrocellulose</td>
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<tr>
<td>Stabilizer</td>
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