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PICATINNY ARSENAL TECHNICAL DIVISION



TECHNICAL REPORT

**SUBJECT: LONG RANGE RESEARCH LEADING TO THE DE-
VELOPMENT OF SUPERIOR PROPELLANTS**

**STUDY NATURE OF DETERIORATION OF M1 CANNON
PROPELLANTS OF LOW HYGROSCOPICITY UNDER MAG-
AZINE STORAGE CONDITIONS**

PROJECT NO. TA1-5008B, ITEM C REPORT NO. 2

**PREPARED BY: H. A. AARONSON
 H. J. JACKSON**

DATE: 30 OCTOBER 1953

P. A. SERIAL NO. 1972

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LONG RANGE RESEARCH LEADING TO THE
DEVELOPMENT OF SUPERIOR PROPELLANTS

Study Nature of Deterioration of M1 Cannon
Propellants of Low Hygroscopicity under Magazine Storage Conditions

Project No.: TAL-5006B, Item C

Report No. 2

Picatinny Arsenal Technical Report No. 1972

Date: 30 October 1953

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Project No.: TAL-5006B - Item C
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Project Title: Long Range Research Leading to the
Development of Superior Propellants -
Study Nature of Deterioration of M1
Cannon Propellants of Low Hygroscopicity
under Magazine Storage Conditions.

OBJECT

To continue storage, at ambient temperature, of selected propellant lots previously studied under this project and to note if (1) any visible evidence of deterioration develops, and (2) methyl violet paper is suitable for indicating instability of these propellants.

To continue the 65.5°C Surveillance Test on the selected propellant samples.

ABSTRACT

In 1937 M1 and M3 Propellants, then designated as FNH powders were comparatively new. No propellant of this type had as yet shown any evidence of instability, and it was not known how such instability would become evident. What was of special interest was to determine if the deterioration would show up as discolored or spotted grains as in the case of the old pyrocellulose-diphenylamine propellants and also if the bleaching of K/10 Methyl Violet Paper could be used to indicate instability of the newer propellants.

The results of early tests on this project were first reported in Picatinny Arsenal Report No. 1085 dated April 21, 1941. One lot of old type pyrocellulose propellant and three lots each of M1 and M3 Propellants were used for study in this program. After heating samples of these lots in a humid atmosphere at 65.5°C and 80°C to brown fumes, the propellant grains showed no evidence of deterioration. Methyl violet paper exposed to these conditions changed to tan and faded gradually. Additional tests were continued to date (1953). The latest 65.5°C Surveillance Tests all required longer times to brown fumes, than originally and show that these propellants which were made between 1927 and 1936 are still fairly stable. This is supported by the results of the analytical determinations

for stabilizer content. Visual inspection of the grains has not shown any discoloration. Also, methyl violet paper exposed to the propellants, stored at ambient temperature for 3 years are still in Class I (unbleached).

The results obtained on the samples used in this project together with observations on many other such propellants since the project was started show that they do not form discolored grains and that the bleaching of methyl violet paper cannot be used to indicate unacceptable stability. Since the objectives of the project have been accomplished, it is recommended that the program be discontinued.

INTRODUCTION:

1. In 1937 an investigation was started to determine whether the then newer type M1 and M3 Propellant Compositions (See Table I) would show some of the same characteristics on deterioration as were observed with the older straight pyrocellulose plus diphenylamine propellant. The particular characteristics of interest were (a) whether some grains of the newer compositions would deteriorate considerably ahead of the others and show this deterioration by changing color or developing spots, and (b) whether N/10 methyl violet paper would detect this deterioration by bleaching (Ref A).

2. A first progress report on this problem, Picatinny Arsenal Technical Report No. 1085, was written in 1941. At that time, no M1 or M3 Propellant had as yet shown any definite deterioration in magazine storage. Three lots of each of these types of propellants and one straight pyrocellulose plus diphenylamine composition were selected for investigation. Samples of these propellants were subjected to elevated storage in dry and moist conditions to accelerate decomposition and periodically inspected. Surveillance Tests at 65.5°C and 80°C as well as tests at 65°C - 95% RH and 80°C - 95% RH were carried to completion without the formation of any visibly deteriorated grains. In all cases the test papers changed to tan or a shade of olive before bleaching. The present report gives the results of additional tests and recent analyses of the stabilizer contents of the propellants.

RESULTS:

3. After an average of 22 years since production, none of the propellants under study has shown any deteriorated or spotted grains after storage at ambient temperature. Surveillance Tests at 65.5°C on these propellants, carried to the development of brown fumes, have not resulted in any discoloration of the grains.

4. Standard N/10 methyl violet papers exposed to the propellants in boxes for three years have not bleached and are still classified as Class I.

5. Analytical data on the change in diphenylamine content from the time of manufacture to 1953 show definite decreases in this stabilizer and the presence of about 0.25% of N-nitrosodiphenylamine plus a few hundredths percent of 2-nitrodiphenylamine. See Table II.

6. The last series of Surveillance Tests at 65.5°C all show a longer time to brown fumes than the first series of tests. See Table III.

DISCUSSION OF RESULTS:

7. Changes in the stabilizer content of the propellants between the time of manufacture and 1953 are shown in Table II. The average age of the propellants at this time is 22 years. In each case the free diphenylamine content had decreased to about 30-50% of the original amount. A portion of the diphenylamine had been converted to N-nitrosodiphenylamine and a few hundredths of a percent to 2-nitrodiphenylamine. However, in each case there was a definite and appreciable loss of stabilizer as shown by the totals in the last column. As is well known, the first conversion products of diphenylamine, such as N-nitroso and 2-nitrodiphenylamine are excellent stabilizers. Experience has shown that a pyrocellulose propellant which retains only about 0.2% diphenylamine still shows quite acceptable stability (Ref B).

8. The latest 65.5°C Surveillance Tests on each of the propellants gave a longer time to brown fumes than the initial tests. This is a very common occurrence which has been discussed in other reports and is probably due to the better stabilizing action of the derivatives of diphenylamine in comparison with diphenylamine itself. The latest results obtained in the 65.5°C Surveillance Tests show that these propellants can be expected to last for quite a few more years, if stored at ambient temperature, before they will have deteriorated to the point of being hazardous. As pointed out in paragraph 3 of the introduction to Picatinny Arsenal Technical Report No. 1085, the M1 and M3 Propellants do not have the black color, which by contrast renders easily visible any orange spots of nitro derivatives of diphenylamine. It would therefore be improbable that such propellants would exhibit the visual evidence of decomposition found in deteriorated pyrocellulose propellant grains of the old type. This surmise has been borne out by the accumulated evidence of observation over the years since the M1 and M3 Propellants were first made. It is thus not unexpected that the six propellants under observation, which still show good stability, have not developed any discolored grains even when subjected to the 65.5°C Surveillance Test to the point of development of brown fumes.

9. Tests with N/10 methyl violet papers on samples of the six M1 and M3 lots studied in this program have not shown any bleaching when the propellants were stored at ambient temperature. Thus, papers exposed to these propellants in 150 lb boxes for the last three years are still in Class I (unbleached). However, over a period of years a number of cases have been found by field inspectors where propellants of these types have produced bleaching of methyl violet papers. These cases were immediately reported to Picatinny Arsenal and Surveillance Tests at 65.5°C made to check for possible instability. Invariably the results of these tests showed that the propellants were far from being in a hazardous state of instability, thus showing that the bleaching of N/10 methyl violet paper is not a satisfactory indication of approaching instability of the

propellant. Based on the present stabilizer content and latest 65.5°C Surveillance Tests as pointed out above, it will very probably be quite a few years before even the slight deterioration necessary to affect the methyl violet paper takes place.

10. At higher temperatures, such as 65.5°C, the methyl violet paper is also an unsatisfactory indicator of approaching instability of M1 and M3 Propellants. This was reported in the first report on this project, PA 1085. In the 65.5°C Surveillance Tests the methyl violet papers first turned to a tan and then this color slowly faded out while the samples still showed excellent stability.

11. The original questions which formed the basis of this project, viz., whether M1 and M3 Propellants would develop spotty grains when deteriorated and whether the bleaching of N/10 methyl violet paper could be satisfactorily used as an end point of stability, have both been answered in the negative. In view of these definite answers, further tests and continued work on this project are considered unnecessary.

CONCLUSIONS:

12a. M1 and M3 Propellants do not develop spotted or discolored grains on deterioration.

b. The bleaching of methyl violet paper is not a satisfactory indicator for the instability of M1 and M3 Propellants.

RECOMMENDATIONS:

13. Since the information sought relative to the formation of discolored grains and the suitability of methyl violet paper for detecting the instability of M1 and M3 Propellants has been obtained, it is recommended that the project be discontinued.

EXPERIMENTAL PROCEDURE:

14. Standard 65.5°C Surveillance tests were conducted on samples of each of the propellants included in this project. Standard N/10 methyl violet indicator papers were exposed, in a standard 150 lb propellant container, to each of the propellants. These papers were inspected for bleaching or change of color at periodic intervals. Samples of each of the propellants, which had been stored at ambient temperature since manufacture, were analyzed for diphenylamine, N-nitrosodiphenylamine and 2-nitrodiphenylamine according to the procedure of Schroeder, Ind. Eng. Chem. v 41 pp. 2818-2827, December 1949.

REFERENCES:

- A. O.O. 471.5/8078, ORDBE 471.5/1413 - 1938; Basic letter and Indorsements. The 3rd paragraph of the 2d Indorsement states the information desired.
- B. Picatinny Arsenal Technical Report No. 448, "Complete Study of the Stability Life of 13 Lots of Smokeless Powder. Eleventh Series of Annual Tests." See paragraph 6.

INCLOSURES:

Tables I, II, III

TABLE I

Composition of M1 and M3 Propellants

<u>Component</u>		<u>M1</u>	<u>M3</u>
Nitrocellulose*	%	85	79
DNT	%	10	-
TNT	%	-	15
Dibutylphthalate	%	5	-
Triacetin	%	-	5
Diphenylamine	%	1	1

*Nitrogen content 13.15% for M1 and 12.6% for M3

TABLE II

Effect of Magazine Storage on Stabilizer Content of Propellants

Lot No.	Type of Composition	Year of Mfr.	Weapon	DPA original %	1953 Stabilizer Content			Total Stab, %
					DPA %	N-nitroso-DPA, %	2-Nitro DPA, %	
PA R3570	Pyrocellulose	1932	75 mm G.	1.0	0.37	0.32	0.06	0.75
DP X3606	M1	1927	75 mm G.	0.99	0.30	0.25	0.05	0.60
DP X3670	M1	1930	75 mm G.	0.91	0.32	0.25	0.05	0.62
DP X3674	M1	1931	75 mm P.H.	0.91	0.32	0.25	0.05	0.62
PA X3837	M3	1936	75 mm G.	0.82	0.42	0.28	0.04	0.74
PA X3855	M3	1936	75 mm G.	0.91	0.36	0.23	0.03	0.62
PA X3856	M3	1936	75 mm G.	0.92	0.44	0.31	0.02	0.77

TABLE III

Initial and Latest 65.5°C Surveillance Tests

<u>Lot No.</u>	<u>65.5°C Surveillance Test* (days)</u>	
	<u>Initial</u>	<u>Latest</u>
DP X3606	1338	2038
DP X3670	1671	1775
DP X3674	1573	1805
PA X3837	719	843
PA X3855	1189	1808
PA X3856	1289	1749

* No grains showed discolorations, spots or other evidences of deterioration. Lots PA X3855 and PA X3856 showed some distorted grains.