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METHOD OF TESTING PROPELLANT STABILITY

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to a method for testing the stability of smokeless powder. More specifically the invention relates to an improved method involving the use of test paper for detecting the excessive decomposition of smokeless powder.

Historically litmus paper was the first indicator used in stability tests on smokeless powder. Many difficulties were experienced with both with the procurement of uniform dye lots and in the handling of the test paper and the indicator was not considered to be satisfactory.

Attempts were made to detect excessive decomposition of the pyrocellulose powder by incorporating rosaniline dye into the powder. Instability of the powder was indicated by a bleaching of the powder grain from pink to white. The introduction of diphenylamine into the powder as a stabilizing agent, however, darkened the powder grains to such an extent that an internal indicator could not be used.

Methyl violet indicator paper was subsequently adopted and gave satisfactory performance with the straight pyrocellulose propellant powders in common use and its use was extended to a wide variety of propellants and explosives with good results. This methyl violet indicator paper was filter paper into which had been absorbed a mixture of para rosaniline acetate and methyl violet dyes and was placed in a sealed container with a propellant specimen and observed at regular intervals to detect fading which was used as an indication of the decomposition of the powder.

With the introduction of double-base and triple-base propellants, however, it became apparent that this indicator was no longer effective with these and other types of non-hygroscopic propellants due to premature fading. The reason for this premature fading is not definitely established but it is known that nitrogen oxide gas is produced in the decomposition of the powder. As this gas escapes from the powder it is oxidized by the atmosphere of the container to form nitrogen dioxide. This nitrogen dioxide gas reacts with the indicator paper and with the stabilizer incorporated into the powder. The portion of the gas reacting with the stabilizer and other components of the powder may be regenerated as nitrogen oxide by reduction and again enter these reactions. Relatively short periods of exposure of the indicator to these propellants was sufficient to effect a complete loss of color. This premature fading has resulted in general unreliability of the tests and necessitated the performance of numerous confirmatory tests. With certain types of propellants this tendency to change color while the propellant was yet stable caused the indicator paper tests to be abandoned.

An indicator paper test for indicating the decomposition of pyrocellulose powder is, however, highly desirable because the presence of even a small quantity of

nitrogen dioxide accelerates the decomposition of pyrocellulose powders. This decomposition may become autocatalytic and result in spontaneous ignition of the powder. Incorporation into the powder of compounds such as diphenylamine or centralite serve to combine with the NO_2 gas produced by the normal decomposition of the powder in the early stages. When decomposition becomes more rapid, however, these compounds cannot combine with the gas at the rate it is produced. Early detection of the presence of an excess of nitrogen dioxide resulting from excessive powder decomposition, therefore, is important as a safety measure so that the propellant may be segregated and destroyed. Such decomposition, when undetected, has caused the loss of ships and storage magazines through spontaneous ignition.

It is an object, therefore, of this invention to provide a method of testing propellant stability which involves an indicator paper for use in ambient temperature surveillance testing which would readily detect nitrogen dioxide gas resulting from excessive powder decomposition but which would resist any color change for a reasonable period when stored with a powder of unquestioned stability.

Other objects will become apparent to those skilled in the art as the invention is disclosed in the following description.

The above objects are obtained in accordance with the invention by the use of an indicator paper impregnated with brilliant green dye. This indicator paper has been found to readily detect nitrogen dioxide gas and at the same time to resist color change in the presence of the various types of propellant powders in service use.

Brilliant green otherwise known to those skilled in the art as tetraethyl-diamino-triphenyl-carbhydride sulfate has the empirical formula $C_{27}H_{34}N_2O_4S$. It is also known as malachite green G, emerald green, solid green, diamond green G and fast green J. It has been used as a dye and as an antiseptic and is known to change from green (alkaline) to yellow (acid) at pH 2.0. Commercially available brilliant green may be used in the indicator papers of the invention.

Any pure white filter paper may be used. The indicator paper is merely drawn through a solution of the brilliant green and air dried. The brilliant green solution may be prepared by dissolving from 1 to 3 grams of the dye (depending upon the concentration desired) in 660 ml. of 95 percent ethyl alcohol plus 40 ml. of glycerin diluted to 1000 ml. with distilled water. After drying the paper is usually cut into strips about 20 mm.×70 mm. and stored in dark bottles until used. The treated paper is a brilliant green color which fades to a white or buff white color.

The brilliant green indicator papers of the invention have been tested in various ways in comparison with N/10 methyl violet papers heretofore utilized in surveillance tests of propellants.

EXAMPLE I

Test strips of brilliant green indicator papers were prepared by dissolving one gram of brilliant green dye in 660 ml. of 95% ethyl alcohol to which 40 ml. of CP glycerin had been added. This solution was diluted to 1000 ml. with distilled water. Sheets of pure filter paper (Schleicher and Schull 598 YD) were drawn through this solution at a uniform rate and air dried. The sheets were then cut into strips 20 mm.×70 mm. and stored in dark bottles.

To test the effects of powder compositions on the stability of the test papers strips of the brilliant green test paper were sealed in quart fruit jars with various

powders of unquestioned stability. These powders were JPN rocket propellant, a centralite stabilized powder, JP rocket propellant, a diphenylamine stabilized powder and cordite N cannon powder, also centralite stabilized. The powder was cut to thin slices and the test papers placed in contact therewith. A specimen of N/10 methyl violet paper was included in each jar for comparison purposes. The jars were stored in a magazine at ambient temperatures and regularly inspected to observe the degree and manner of loss of color.

In 501 tests the brilliant green indicator papers successfully withstood five hundred days of contact with wafers of the stable JPN rocket propellant powder as contrasted with two hundred days for the N/10 methyl violet paper. All of the samples of the N/10 methyl violet papers were faded at two hundred and fifty days whereas only twelve percent of the brilliant green papers had not faded after nine hundred and thirty days.

In 153 tests with JP rocket propellant powder a diphenylamine stabilized ballistite powder the brilliant green indicator paper did not fade in nine hundred and forty days. The N/10 methyl violet paper, however, began to fail at five hundred days and in eighty-one percent of tests had completely faded at nine hundred and forty days.

In 108 tests with Cordite N, a powder containing 18 percent nitroglycerin and 7 percent centralite, the brilliant green papers had not faded after 900 days while the N/10 methyl violet papers had faded in 350 days.

EXAMPLE II

Test strips of the brilliant green indicator paper, prepared as in Example I, were suspended in large glass jars above ten pound samples of the various powders. A specimen of N/10 methyl violet indicator paper was included in each jar and frequent inspections made. Where JPN rocket propellant powder was employed some of the methyl violet papers were bleached after 80 days and all were completely faded after 330 days. In contrast, the brilliant green papers withstood 300 days of storage and only six percent showed a complete loss of color at 340 days.

EXAMPLE III

The sensitivity of the brilliant green indicator paper prepared as in Example I to unstable powder was evaluated by sealing the indicator strips in sealed glass tubes with a measured quantity of NO_2 gas so that the amount of gas required to react completely with the indicator was measured. Nitrogen oxide gas was generated in a duPont nitrometer and transferred to a calibrated measuring burette. A sample tube containing a strip of test paper was connected to the burette. A measured amount of NO_2 gas was admitted to the evacuated sample tube and the system permitted to reach atmospheric pressure by the addition of air. The sample tube was then sealed off with a torch and stored away from light between observations. Table I indicates the observed results with N/10 methyl violet papers as a control:

Table I

COMPARISON OF THE EFFECT OF DEFINITE QUANTITIES OF NITROGEN DIOXIDE GAS ON BRILLIANT GREEN AND N/10 METHYL VIOLET INDICATOR PAPERS

	Brilliant Green Indicator Paper (Conc. of Dipping Solution 1 gm/liter)			N/10 Methyl Violet Indicator Paper		
	Ml. of Nitrogen Dioxide	Estimated Percent Fading in 17 Hours	Estimated Percent Fading in 90 Hours	Ml. of Nitrogen Dioxide	Estimated Percent Fading in 17 Hours	Estimated Percent Fading in 90 Hours
Test No. 1, Sample 1	0.04	0	0	0.05	5	5
Test No. 1, Sample 2	0.05	0	0	0.15	75	90
Test No. 1, Sample 3	0.08	0	0	0.23	100	100
Test No. 1, Sample 4	0.20	100	100	0.31	100	100
Test No. 1, Sample 5	0.48	100	100	0.48	100	100

EXAMPLE IV

The sensitivity of the brilliant green indicator paper prepared as in Example I to unstable powder was measured by exposure to an atmosphere where the concentration of NO_2 gas was increasing by small increments. Approximately one hundred grams of naturally aged pyro powder was placed in the bottom of a large desiccator and used as a source of supply of NO_2 gas. The powder used was decomposed to such an extent that the 65.5° C. surveillance was about thirty days. The indicator papers were suspended in the desiccator from a specially constructed lid. N/10 methyl violet test papers were used as controls. Table II indicates the results observed:

Table II

RELATIVE TIME REQUIRED TO FADE BRILLIANT GREEN INDICATOR PAPERS BY UNSTABLE PYRO POWDERS (N/10 METHYL VIOLET PAPER EQUALS 100 PERCENT)

Concentration of dye, gm./liter	Test No. 1	Test No. 2	Test No. 3	Test No. 4	Test No. 5
1 percent	91	83	94	100	60
3 do	100	116	105	233	100
5 do	118	217	(1)	(1)	(1)

[1] End points not sufficiently definite.

Table III shows the results of compatibility tests performed at 65.5° C. on methyl violet and brilliant green indicator papers with JP and JPN ballistite.

Table III

COMPATIBILITY OF BRILLIANT GREEN AND METHYL VIOLET INDICATORS WITH JP AND JPN BALLISTITE AT 65.5° C.

JP Ballistite [1]	Time to Color Change		JPN Ballistite [2]	Time to Color Change	
	N/10 Methyl Violet	Brilliant Green		N/10 Methyl Violet	Brilliant Green
	Days	*Days*		*Days*	*Days*
I. H. mk 1 Lot 400	7	11	I. H. mk 1 Lot 1795	4	10
I. H. mk 1 Lot 400	7	11	I. H. mk 1 Lot 1795	4	10
I. H. mk 1 Lot 400	7	11	I. H. mk 1 Lot 1795	4	10
I. H. mk 1 Lot 405	7	8	I. H. mk 1 Lot 1801	4	10
I. H. mk 1 Lot 405	7	8	I. H. mk 1 Lot 1801	4	10
I. H. mk 1 Lot 444	5	8	I. H. mk 1 Lot 1804	4	9
I. H. mk 1 Lot 530	7	11	I. H. mk 1 Lot 1804	4	10
I. H. mk 1 Lot 590	5	7	I. H. mk 1 Lot 1804	4	11
I. H. mk 1 Lot 590	5	6	I. H. mk 1 Lot 1809	4	9
I. H. mk 1 Lot 1010	6	6	I. H. mk 1 Lot 1809	4	11

45 grams of powder were used in each test.

[1] End point yellow due to exudate from powder.
[2] All papers to white end point.

From the results of the above it may be seen that brilliant green indicator paper prepared according to the invention is decidedly superior to methyl violet paper. The brilliant green papers of the invention have been found to be stable for long periods in the presence of the various powders presently in service use as rocket and gun propellants but still sensitive to the presence of an excess of the NO_2 gas resulting from the advanced decomposition of these powders.

It is to be understood, however, that the invention may be practiced otherwise than as specifically described within the scope of the following claims.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. The method of continuously testing the stability of nitrocellulose containing propellants by detecting the presence of nitrogen dioxide gas which includes the steps of impregnating paper with tetraethyl-diamino-triphenylcarbhydride sulfate whereby the paper is dyed green; placing the impregnated paper in close proximity to the propellant to be tested; and leaving the paper in close proximity to the propellant until the green color begins to fade.

2. The process of claim 1 in which the paper is impregnated by immersion in a solution of the sulfate, followed by drying to get rid of the solvent.

3. The process of claim 2 in which one to three grams of sulfate are dissolved in a mixture of about 660 milliliters of 95% ethyl alcohol, about 40 milliliters of glycerin, and about 300 milliliters of water.

References Cited in the file of this patent

Venkataraman, The Chemistry of Synthetic Dyes, vol. II, p. 1327, Academic Press, Inc., New York, 1952.

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