United States Patent Office

2,698,228

Patented Dec. 28, 1954

2,698,228

FLASHLESS PROPELLANT

John F. Kincaid, Jefferson Township, Allegheny County, and Russell C. McGill, Baldwin Township, Allegheny County, Pa., assignors to the United States of America as represented by the Secretary of the Navy

No Drawing. Application December 30, 1944, Serial No. 570,808

5 Claims. (Cl. 52—13)

The present invention relates to propellants and more particularly to new and improved essentially flashless propellants suitable for large caliber guns and cannon.

It has long been recognized that during military and naval operations carried out at night, an essentially flashless propellant should be used in order to obviate brilliant muzzle flash that might reveal the friendly gun position or momentarily blind command and fire control personnel in the vicinity of the weapon. Within recent years, British experimenters have made great strides in solving this problem by incorporating a substantial proportion (about 55%) of nitroguanidine in a double base or "Cordite" type of powder. The resulting composition (referred to generally as "Cordite-N") is essentially flashless when fired in large caliber cannon and has a force approximately equivalent to that of Pyro powder.

Nevertheless, like other double base powders of the prior art, Cordite-N, while far superior from the viewpoint of flash, suffers from the disadvantage that it contains a volatile high potential plasticizer, namely nitroglycerine. Under conditions of high temperature storage, this volatile component tends to vaporize with the result that the ballistic properties of the powder may undergo a significant change during storage. In addition, under the conditions prevailing in air conditioned and ventilated powder magazines on modern naval vessels, the nitroglycerine in double base powders exhibits a demonstrable tendency to distill, thereby creating a potential hazard due to the possible condensation of a highly sensitive explosive at various points in the magazine and ventilating system. For these reasons, Cordite-N, while far superior to Pyro in respect to flash, does not represent the ideal solution to the flash problem.

The principal object of the present invention is to provide a new and improved essentially flashless gun powder.

Another object is the provision of a gun or cannon powder having the desirable flashless characteristics of Cordite-N without the disadvantages associated with a double base powder that contains a volatile high explosive plasticizer for the nitrocellulose component of the propellant.

A further object is to provide a commercially feasible method of preparing an essentially flashless non-hygroscopic propellant that does not materially alter in ballistic properties when stored at high temperatures.

Other objects and advantages will be apparent as the invention is hereinafter more particularly described.

In accordance with the present invention, it has been found that the foregoing objects may be accomplished by substituting certain relatively non-volatile explosive nitric esters for the nitroglycerine heretofore employed as a nitrocellulose plasticizer in a Cordite-N type of cannon powder. More particularly, the improved propellant of the present invention consists of a modified double base type of powder comprising:

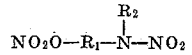
(1) Nitrocellulose,

(2) An essentially non-volatile thermally stable explosive nitric ester capable of plasticizing the nitrocellulose, and

(3) A sufficient proportion of nitroguanidine to render the finished propellant essentially flashless when fired in a large caliber gun or cannon.

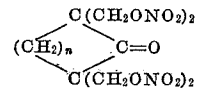
The nitrocellulose plasticizers employed in accordance with the present invention may for example consist of the essentially non-volatile members of the following illustrative classes of compounds that are capable of plasticizing nitrocellulose, namely:

(*a*) Nitroxyalkyl nitramines having the general structural formula:



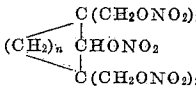
where R_1 is an alkylene group and R_2 is a nitroxyalkyl group or an alkyl group;

(*b*) Polynitrate esters of polymethylolcycloalkanones of the general formula:



where *n* is a small whole number; and

(*c*) Polynitrate esters of polymethylolcycloalkanols of the general formula:



where *n* is a small whole number.

As illustrative examples of the foregoing types of non-volatile explosive nitric esters, the following specific compounds may be mentioned purely by way of illustration; bis(2-nitroxyethyl)nitramine (hereinafter called "DINA"), tetramethylolcyclopentanone tetranitrate (hereinafter called "Fivonite"), tetramethylolcyclopentanol pentanitrate (hereinafter called "Fivolite"), tetramethylolcyclohexanone tetranitrate (hereinafter called "Sixonite"), and tetramethylolcyclohexanol pentanitrate (hereinafter called "Sixolite").

I. PREPARATION OF THE NON-VOLATILE PLASTICIZERS

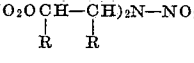
The preparation of DINA, as described and claimed in the copending applications of Wright and Chute, Serial Nos. 570,813, now Patent No. 2,461,582 and 570,814, now Patent No. 2,462,052, and Blomquist and Fiedorek, Serial No. 570,804, now Patent No. 2,678,946, all filed of even date herewith, may be accomplished by the dehydration of the bis(nitroxyalkyl)amine nitrate obtained by nitrolysis of the appropriate dialkanolamine; for example:

(*a*) $(HOCH_2CH_2)_2NH \xrightarrow{HNO_3} (NO_2OCH_2CH_2)_2NH\cdot HNO_3$

(*b*)

$(NO_2OCH_2CH_2)_2NH\cdot HNO_3 \xrightarrow[\text{(chloride catalyst)}]{(Ac)_2O} (NO_2OCH_2CH_2)_2N{-}NO_2 + H_2O$

Certain homologues of DINA of the type:



where one R is an alkyl group and the other hydrogen may be prepared in a similar manner from higher homologues of diethanolamine, as described and claimed in Blomquist and Fiedorek application, Ser. No. 570,805, now Patent No. 2,481,283, also filed of even date herewith. Certain analogues of DINA of the type:

$$(NO_2O{-}CH_2{-}CH_2){-}N(R){-}NO_2$$

where R is an alkyl group, obtained in a similar manner from the appropriate secondary alkanolalkylamine, are described and claimed in another copending application of Blomquist and Fiedorek, Ser. No. 570,804, also filed of even date herewith.

The plasticizers of the class represented by Fivonite, Fivolite, Sixonite and Sixolite are prepared as described in the literature (Ger. Pat. 509,118; Br. Pat. 345,859; U. S. 1,962,065; compare Davis, The Chemistry of Powder and Explosives, John Wiley and Sons, 1943, vol. II, page 285).

II. PREPARATION OF THE PROPELLANT

In preparing the improved propellant of the present invention, any suitable procedure heretofore used for the preparation of double base powders such as Cordite-N may be used, with the exception that one or more of the above identified relatively non-volatile nitrocellulose plas-

ticizers are substituted for the nitroglycerine employed in the prior art propellants. Thus the powders of the present invention may be made in conventional "solvent-extrusion" equipment without material alteration of the procedural steps heretofore employed in the production of double base powders containing a substantial proportion of nitroguanidine.

The amount of non-volatile plasticizer required for the present propellants will depend in part on the nature of the particular plasticizer and other components selected and in part upon the characteristics desired in the finished powder. In general, however, satisfactory powders may be made using approximately the following proportions of ingredients:

	Per cent
Nitrocellulose	15 to 35
Non-volatile explosive plasticizer	15 to 35
Nitroguanidine	70 to 30

In order more clearly to disclose the nature of the present invention, several specific examples will be described in detail below. It should be clearly understood, however, that the examples are purely illustrative of the fundamental principles involved and are in no sense intended either to delineate the breadth or scope of the invention or to limit or restrict the ambit of the appended claims.

EXAMPLE I.—PREPARATION OF A PROPELLANT CONTAINING DINA AS AN NG SUBSTITUTE

As an example of the use of DINA as a nitroglycerine substitute in nitroguanidine propellants, there is described below a powder having approximately the same thermochemistry and flash properties as British Cordite-N.

In the preparation of this powder regular commercial gun-cotton (13.4% N) was used. The nitrocellulose was dehydrated by the usual commercial process of forcing alcohol through a water wet block of nitrocellulose and pressing to a known alcohol content. The nitrocellulose was dehydrated to contain less than the quantity of alcohol necessary for the proper solvent ratio, and the additional alcohol added to the mixer with the other solvent.

The nitroguanidine was obtained from the Welland Chemical Works at Niagara Falls, Canada, and was the conventional grade used in the manufacture of British Cordite-N. The nitroguanidine as received was a dry, finely divided, crystalline powder.

The sample of DINA used was prepared from diethanolamine using the procedure described and claimed in the copending application of Wright et al., Serial No. 570,813, now Patent No. 2,461,582, filed of even date herewith. The centralite and solvents used were of the grade normally employed in smokeless powder manufacture. The Chemical designations of Centralite I (diethyldiphenyl urea) and Centralite II (dimethyl diphenyl urea) may be found in the handbook, "The Chemistry of Powder and Explosives" by Tenney L. Davis, published by John Wiley and Sons, Inc. (1943), in volume II at page 319.

The solvent used was a mixture of 75% acetone and 25% alcohol. The mixture was selected because of the solubility characteristics of the solid explosive.

The composition of a typical propellant made with DINA was as follows:

	Per cent
Nitrocellulose (13.4% N)	20.0
Nitroguanidine	55.0
DINA	19.0
Centralite #1	6.0

The weight of solvent used was 20% of the dry weight of the mixture.

The alcohol-wet nitrocellulose together with the extra alcohol was mixed for five minutes in a counter-rotating sigma blade mixer with cold tap water circulating through the jacket. The dry nitroguanidine was added and mixing continued for another five minutes. At this point in the mixing cycle the acetone solution of DINA was added and mixing continued for thirty minutes while water at 45° C. was circulated through the jacket. Then the ethyl centralite was added and mixing continued for forty-five minutes. Finally, with cool water (20° C.) flowing through the jacket, mixing was continued for fifteen minutes, making a total mixing time of 100 minutes.

After mixing, the dough was quite soft and rather cheesy in appearance. The dough was blocked at approximately 4,600 lbs./in.^{2} and then extruded through an 0.276" die at a pressure of approximately 3000 lbs./in.^{2} using two 50 mesh screens. The powder was cut green to the proper length, tied in bundles and dried in an electric oven for one day at 30° C. and fourteen days at 45° C.

Other experimental compositions have been prepared successfully using pyrocotton and various mixtures of guncotton and pyrocotton. Different solvent proportions (between 50%–50% and 80%–20% acetone-alcohol) have also been found satisfactory. Experiments have also been made with shorter mixing cycles and different water jacket temperatures. For most preparations a spaghetti process has also been found advantageous to remove clumps of uncolloided nitrocellulose and poorly mixed material as well as contributing to the mechanical work done on the colloid.

EXAMPLE II.—PREPARATION OF PROPELLANT CONTAINING FIVONITE AS AN NG SUBSTITUTE

The following description will serve as an example of the use of Fivonite as a nitroglycerine substitute. The composition was chosen again so that the finished powder would have approximately the same thermochemistry and flash properties as British Cordite-N.

The composition of a typical propellant made with Fivonite was as follows:

	Per cent
Nitrocellulose (13.4% N)	23.0
Nitroguanidine	55.0
Fivonite	19.0
Centralite #1	3.0

The Fivonite may be prepared in ordinary laboratory equipment by the procedure described in the literature. The other ingredients were the same lots that were used in Example I.

The compounding procedure for this sample was also the same as that used for the DINA composition described in Example I.

EXAMPLE III.—PREPARATION OF A PROPELLANT CONTAINING SIXONITE AS AN NG SUBSTITUTE

The following description will serve as an example of the use of Sixonite as a nitroglycerine substitute. The composition was likewise chosen to have the same thermochemistry and flash properties as British Cordite-N.

The composition of a typical propellant made with Sixonite was as follows:

	Per cent
Nitrocellulose (13.4% N)	23.0
Nitroguanidine	55.0
Sixonite	20.0
Centralite #1	2.0

The Sixonite may be prepared in ordinary laboratory equipment by the procedure described in the literature. The other ingredients were the same lots that were used in Example I.

The compounding procedure, amount of solvent, and solvent composition were the same as in Example I.

The use of certain non-explosive plasticizers in a Cordite-N type of propellant is described and claimed in the copending application of Holmes and Lawson, Ser. No. 524,638, filed March 1, 1944, now abandoned.

III. PROPERTIES OF THE PROPELLANTS

The propellants of the present invention, prepared as illustrated in the foregoing examples, are characterized by three particularly outstanding properties, namely (1) flashlessness, (2) low volatility, and (3) low hygroscopicity.

1. Flashlessness

Considering firstly the flash characteristics of the present powder, this property is strikingly shown in the tests summarized in Table I. All the propellants employed in these tests were used in charges that gave essentially the same velocities in a 6"/47 worn naval gun (ca. 2725 ft./sec.), a large quantity of decoppering agent (lead foil) being employed with each charge in order to increase the probability of flash. The summary in Table I indicates the percent of flash produced by a given test powder when 250 grams of lead foil was used with each charge as a decoppering agent. A similar test was made using a still larger quantity (450 g./charge) of decoppering agent per charge in order to increase the severity of the conditions. The flash results obtained in both of these tests, as determined on the basis of the photographic results, are summarized in Table I.

TABLE I

Powder	Flash: Percent of Flash of Normal Pyro Powder (average)	
	225 g., Pb foil	450 g., Pb Foil
	Percent	*Percent*
Standard Pyro	100	100
Pyro containing 4.4% K_2SO_4	33	72
Cordite N/P/M [1] added K_2SO_4	4	16
DINA Powder [2]	0	9
Fivonite Powder [3]	0	0

[1] Cordite N/P/M had the following composition: nitro-cellulose (13.1% N), 18.70%; nitroglycerine, 18.20%; nitroguanidine, 53.80%; centralite-1, 7.4%; cryolite, 0.30%; and K_2SO_4, 1.50%.

[2] DINA powder consisted of 20 parts pyronitrocellulose, 55 parts nitroguanidine, 19.5 parts DINA, 1.5 parts centralite-1, 4 parts dibutylphthalate and 1.5 parts K_2SO_4 (added).

[3] The "Fivonite Powder" consisted of 25 parts pyronitrocellulose, 54 parts nitroguanidine, 17.5 parts Fivonite, 1.5 parts centralite-1, 2 parts dibutylphthalate and 1.5 parts K_2SO_4 (added).

2. Non-volatility

The non-volatility of the powders of the present invention compared with the relatively high volatility of Cordite-N was indicated by placing ¼" single perforated grains of several test powders in open dishes, subjecting them to an elevated temperature and determining their weight-loss as a function of time. An initial rapid loss (corresponding to the residual solvent content of the powder) was disregarded. The comparative data are given in Table II.

TABLE II

Explosive Plasticizer in Test Powder	Percent Explosive Plasticizer in Powder	Percent Wt. Loss per hr. at 100° C.	Percent Wt. Loss per day at 65° C.
Nitroglycerine	18.5	0.25	0.57
DINA	19.0	0.030	0.020
Fivonite	18.0	0.012	0.019

Further evidence regarding volatility was obtained in surveillance tests carried out at 78° C. After 3 weeks storage, a considerable amount of nitroglycerine had condensed inside a bottle containing Cordite-N. In contrast, a DINA powder, after six months similar storage exhibited only a trace of distilled explosive while a Fivonite powder showed no trace of distilled explosive whatsoever.

3. Low hygroscopicity

The hygroscopicity of the present powders compared with that of so-called "non-hygroscopic" (NH) powder and "Pyro" powder was determined by storing test samples in atmospheres of controlled humidity and then periodically weighing the samples until equilibrium was definitely attained. The data are given in Table III.

TABLE III

Sample	Percent Hygroscopic Moisture, at 30° C.		
	20% RH	70% RH	90% RH
(1) DINA powder	0.03	0.19	0.31
(2) Fivonite powder	0.01	0.16	0.25
(3) "NH" Powder	0.25	0.65	1.05
(4) "Pyro" Powder	0.50	1.50	2.50

It will be seen from the data in Table III that the powders of the present invention are definitely superior to "NH" and "Pyro" powders in respect to hygroscopicity. Indeed, the present powders open the possibility of shipping and storing propellants of this type in relatively cheap wooden boxes.

4. Other advantageous properties

It should be mentioned that the DINA plasticized powders and the Fivonite plasticized powders of the present invention possess certain individual characteristics in addition to their common class characteristics: that is to say, the DINA powders differ in certain important respects from the Fivonite powders. Thus, for example, the DINA plasticized powder is somewhat superior to the Fivonite plasticized powder in respect to drying time and impact strength. For these and other reasons, the DINA powder may be preferred over the Fivonite powder for certain specific applications. Nevertheless, for other specific applications, the Fivonite powder may prove to be somewhat more satisfactory in other respects.

It will be evident from the data discussed above that the propellants of the present invention are characterized by a number of highly advantageous properties that render them particularly attractive when compared with some of the best powders of the prior art.

It will also be apparent to those skilled in the art that many variations may be made in the detailed procedure set forth in the foregoing specific examples. Thus the proportions of ingredients or the preparative conditions described in the examples may be changed within wide limits. In some cases it may be desirable to incorporate additional propellant components, or to add additional steps, or to eliminate certain steps described in the example. In other cases it may be desirable to employ more than one non-volatile explosive plasticizer, or to use a mixture of a non-volatile explosive plasticizer and a conventional plasticizer. All such modifications are to be understood as embraced within the scope of the appended claims.

We claim:

1. An essentially flashless, thermally stable propellant suitable for use as a cannon powder, comprising about 15% to about 35% nitrocellulose; from about 15% to about 35% of a non-volatile explosive nitric ester capable of plasticizing said nitrocellulose; and from about 70% to about 30% of nitroguanidine, said explosive plasticizer comprising bis(2-nitroxyethyl)nitramine.

2. An essentially flashless, thermally stable propellant suitable for use as a cannon powder, comprising about 20.0% nitrocellulose, about 55.0% nitroguanidine, about 19.0% bisnitroxyethylnitramine and about 6.0% centralite No. 1.

3. An essentially flashless propellant comprising from 30 to 70 per cent of nitroguanidine and from 15 to 35 per cent of nitrocellulose plasticized with bis(2-nitroxyethyl) nitramine.

4. An essentially flashless thermally stable propellant comprising about 70 to 30 percent nitroguanidine, about 15–35 per cent nitrocellulose, and from about 15 to 35 per cent of a nitroxyalkyl nitramine having the general structural formula

$$NO_2{-}O{-}R_1{-}\underset{\displaystyle R_2}{\underset{|}{N}}{-}NO_2$$

where R_1 is an alkylene group and R_2 is a radical selected from the group consisting of alkyl and nitroxyalkyl.

5. An essentially flashless propellant comprising approximately 55 per cent nitroguanidine, 6 per cent centralite No. 1 and 20 per cent nitrocellulose plasticized with a nitroxyalkyl nitramine having the general structural formula

$$NO_2{-}R_1{-}\underset{\displaystyle R_2}{\underset{|}{N}}{-}NO_2$$

where R_1 is an alkylene group and R_2 is a radical selected from the group consisting of alkyl and nitroxyalkyl.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,454,414	Skilling	May 8, 1923
1,582,256	Franklin	Apr. 27, 1926
1,754,417	Davis	Apr. 15, 1930
1,962,065	Friedrich	June 5, 1934

FOREIGN PATENTS

Number	Country	Date
543,174	Germany	Feb. 2, 1932
578,300	Germany	June 12, 1933