PROPELLANT WITH POLYMER
CONTAINING NITRAMINE MOIETIES AS
BINDER

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ABSTRACT
A novel binder for propellant compositions, and its
method of preparation, said binder being a polymer of
the formula:

\[
\begin{align*}
H \left( \text{OCH}_{2}\text{NCH}_{2}\text{CH}_{2}\text{NCHOCH}_{2}\right) \cdot \text{OH.}
\end{align*}
\]

and novel propellant compositions thereof.

13 Claims, No Drawings
PROPELLANT WITH POLYMER CONTAINING NITRAMINE MOIEITIES AS BINDER

This is a division of application Ser. No. 219,183, filed Jan. 19, 1972, now U.S. Pat. No. 3,808,276.

BACKGROUND OF THE INVENTION

Solid propellants are usually made of the three basic ingredients: (1) oxidizer, (2) fuel, and (3) binder. Two or even three of these may be contained in the same material. A convenient way to divide solid propellants into classes is according to physical state, i.e., homogeneous (single-base or double-base) and composite. A single-base propellant contains nitrocellulose as the main ingredient with a stabilizer such as diphenylamine added, as well as other conventional additives depending on the application. Single-base propellants are used primarily in gun applications and cartridge-actuated devices. Double-base propellants have two principal ingredients — nitrocellulose and nitroglycerine, and may have various conventional ingredients as stabilizers, burning rate modifiers, extrusion lubricants and flash suppressors. When additional oxidizers are added to the double-base propellant, one has a composite modified double-base propellant. Composite propellants are generally composed of an oxidizer and a fuel and/or binder. Well-known oxidizers and fuels are used.

The binder material in composite propellants usually is a polymeric material and nitrocellulose is the most commonly known and used binder component. Thus, nitrocellulose finds wide use in all types of propellant formulations. However, the use of nitrocellulose as a binder in gun propellants results in a high flame temperature and low gas output, both of which are undesirable features. While the replacement of nitrocellulose in gun propellants with a rubber binder gives better flame temperature and gas output, it requires large amounts of output for efficient propellant combustion. Moreover, in solid rocket propellants and other composite propellants, while nitrocellulose offers high energy it generally gives poor low temperature mechanical properties and relatively high sensitivity. The use of a rubber binder for these composite propellants improves the low temperature mechanical properties and sensitivity but such propellants are less energetic and less efficient than those based on nitrocellulose.

SUMMARY OF THE INVENTION

It is an object of this invention to obtain a new binder for propellant compositions, and a method of preparing such a binder.

It is an additional object of the instant invention to obtain a new binder for propellant compositions which has a low flame temperature.

It is a further object of the present invention to obtain a new binder for propellant compositions with a high gas output.

It is still another object of the instant invention to produce propellant compositions which have good low temperature mechanical properties.

It is yet another object of the instant invention to produce a propellant having low sensitivity.

It is still another object of the invention to produce a binder for propellant compositions which is thermally stable.

Still another object of the instant invention is to produce a binder for propellant compositions which is compatible with other propellant ingredients.

It is an additional object of the present invention to produce a binder for propellant compositions which can be used as a replacement for or additive to a nitrocellulose binder.

These and other objectives are accomplished by the use of a new polymer binder which offers the desirable advantages of both nitrocellulose and rubber binders, in solid propellants such as gun propellants and rocket propellants.

The objects, advantages, and novel features of the invention will become apparent from the following detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The novel binder polymer of the instant invention is α-hydro-ω-hydroxy poly (oxymethylenenitramino),

\[ H \rightarrow OCH_2 \text{N} \quad \text{CH}_2 \text{CH}_2 \text{N} \quad \text{CH}_2 \text{CH}_2 \rightarrow \text{OH} \]

and is designated as EDNAP. While any molecular weight polymer will suffice so long as the polymer is operable for binder purposes, it is preferred to use a polymer of a molecular weight of from about 750 to about 3,000, or more preferably from about 1,000 to about 2,500. This type of polymer is synthesized by reacting 1,6-dichloro-2,5-dinitrazahexane (DCDNH) with a polyhydroxy alcohol, exemplified by ethylene glycol. The polymer is thermally stable and can be crosslinked with hexane diisocyanate to form a rubbery gumstock.

A more detailed description of the preparation is as follows. The DCDNH, which reacts with the polyfunctional alcohol, is prepared by reacting ethylene dinitramine with formaldehyde and hydrogen chloride in acetic acid at about 0°C. The DCDNH is usually recrystallized from benzene before preparing the polymer. The bulk reaction between DCDNH and the polyol may be carried out between room temperature and 100°C, but the range of 40°-60°C is preferred. The ratio of hydroxyls to chlorines in the respective reactants is 1.0 to 1.5. Operation under reduced pressure is desirable so as to rapidly remove the hydrogen chloride generated by the reaction and thereby prevent its reaction with the poly-ol. Prior to use in propellant formulations, the prepolymer should be thoroughly washed with base.

EDNAP, when crosslinked, will form a high energy, low glass transition temperature binder which is nearly oxygen balanced and will form low molecular weight products upon combustion. The properties of EDNAP are compared to nitrocellulose and butarez II (a rubber binder) in Table I, below.

| Table I |
|-----------------|------------------|------------------|
| **EDNAP**       | **Nitrocellulose** | **Butarez II**   |
| **(12.6%)**     | **(12.6%)**       | **(12.6%)**      |
| **Empirical**   | **C₈H₁₀N₂O₄**    | **C₉H₁₄N₂O₆**   | **C₈H₈** |
| **Formula**     |                  |                  | 6.7      |
| **ΔHₑ kcal/100**| **−33.4**         | **−58.8**        |          |
| **gms**         |                  |                  |          |
| **Monopropellant*** | **273,000**      | **375,000**      |          |
| **Impetus**     |                  |                  |          |
| **(ft-lb/lb)**  |                  |                  |          |
The low flame temperature and high gas output of EDNAP is ideal for gun propellant applications. For example, propellants with about 20 percent EDNAP as a binder with other well-characterized compounds have calculated impetus of up to 420,000 ft-lb/lb at 2,700°K. This is a 25 percent gain over Olin ball powder which is presently used for many gun propellant applications.

In solid rocket propellants EDNAP also calculates well. For example, Table II shows two formulations which are comparable to composite modified double-base (CMDB) propellants in impulse. The advantages of the EDNAP binder rocket propellants are their expected good low temperature mechanical properties and lower sensitivity compared to the CMDB propellants.

| Table II |
| % Composition | I | II |
| EDNAP | 25 | 20 |
| AP (aluminum perchlorate) | 50 | — |
| Al | 25 | 15 |
| HMX | 65 | 65 |
| Lₚ, sec | 1.895 | 1.852 |
| Density, gm/cc | 0.265 | 0.028 |
| PL | 505 | 505 |
| OL | 0.265 | 0.028 |

In use in solid propellants, the cured polymer is generally used. The polymer can be cured with any conventional curing agent such as any of the crosslinking polyfunctional isocyanates. Exemplary are toluene diisocyanate and hexane diisocyanate, to name just a few of the many conventional crosslinking agents readily available. A wide variety of propellant compositions can be made using the cured prepolymer as the binder. It is preferred to use the EDNAP in double-base and composite type propellants, rather than in single-base propellants. In a composite propellant the amount of EDNAP present is about 10–25 percent by weight of the propellant composition. In these composite types, conventional fuels, such as aluminum, beryllium, zirconium, magnesium, boron, and their corresponding hydrides, as well as lithium, and lithium aluminum hydride, may be used in amounts varying from 0 to 25 percent by weight, preferably at least about 10 percent by weight. Conventional oxidizers, such as cyclotetramethylene tetranitramine (RDX), and ammonium and alkali metal nitrates or perchlorates may be present in amounts ranging from about 55 to 90 percent. With respect to the latter, it would be preferable to have from 55 to 80 percent of oxidizer because it is desired to have at least 10 percent of fuel present in the composition, although the propellants would be operative in the absence of the fuels. In addition to the oxidizer, EDNAP and fuel, any of the conventional additives such as plasticizers, curing agents, stabilizers, burning rate additives, catalysts, etc., are also possible components of the composite formulation. The amount of curing agent necessary to crosslink the polymer is not critical and generally conventional amounts of about 1 to about 6 percent will suffice. With respect to the amount of plasticizer present, usually the EDNAP may be plasticized with up to twice its weight with energetic materials like nitroglycerine or diethylene glycol dinitrate.

In a double-base type propellant, a satisfactory propellant can be obtained by replacing up to about one half of the nitrocellulose with EDNAP. Thus, while the typical double-base propellant will contain about 30–50 percent by weight of a high energy explosive such as nitroglycerin, diethylene glycol dinitrate, methyl trimethylolmethane trinitrate or others, and about 40 to about 60 percent of nitrocellulose, the propellant compositions of the instant invention will contain from about 1 to about 30 percent of EDNAP, replacing up to about one half of said nitrocellulose, usually present in the conventional type. The resulting propellant will have the polymer present in an amount equal to or less than the amount of nitrocellulose present. Conventional additives, such as plasticizers (phthalates, triacetin, etc.), stabilizers (2-nitrophellulanine, tertiary butyl catechol, etc.), burning rate modifiers (lead salts, etc.), extrusion lubricants (stearates, soaps, etc.), and flash suppressors (potassium salts, etc.) may also be added.

The following examples illustrate the method of obtaining the novel polymer as well as some propellant formulations utilizing the novel polymer.

**EXAMPLE I**

0.6 moles of DCDN, 0.56 moles of ethylene glycol, and 0.11 moles of glycerol were reacted at 50°–60°C for 24 hours at the low pressure level produced by a water aspirator. The cooled reaction mixture was dissolved in methylene chloride and washed successively with water, sodium bicarbonate solution, and finally sodium hydroxide solution. For drying, benzene was added to the solution and the total solvent was distilled. Last traces of solvent were removed by sparging with dry nitrogen at 60°C. The product, on analysis, was found to contain 0.19 percent water and to have an hydroxyl equivalent weight of 572.

**EXAMPLE II**

A propellant formulation was prepared in the laboratory of the following composition:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum</td>
<td>12</td>
</tr>
<tr>
<td>HMX</td>
<td>65</td>
</tr>
<tr>
<td>EDNAP</td>
<td>19.2</td>
</tr>
<tr>
<td>HDI (hexamethylene diisocyanate)</td>
<td>3.8</td>
</tr>
</tbody>
</table>

This composition has a calculated specific impulse of 265 seconds and a density of 0.065 lbs/in³. Its burning rate at 1,000 psi was 0.21 in/sec.

**EXAMPLES III-IV**

The two formulations set forth at Table II, supra, are additional examples of propellant compositions in which EDNAP is incorporated.
Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described herein.

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

1. A solid propellant composition which contains a cured polymer as a binder component therefor, said polymer being of the formula:

\[
\begin{align*}
H &\rightarrow OCH_2CH_2N CH_3O CH_2CH_2 \rightarrow OH. \\
\text{NO}_2 &\quad \text{NO}_2
\end{align*}
\]

2. The solid propellant composition of claim 1, wherein said composition is a composite type solid propellant comprising a propellant oxidizer and said polymer.

3. The composite type solid propellant of claim 2 comprising an oxidizer, a fuel, and said polymer.

4. The composite type solid propellant of claim 3 comprising from about 55–80 percent by weight of said oxidizer, from about 10 to about 25 percent by weight of said fuel, and from about 10 to about 25 percent by weight of said polymer.

5. The composite type propellant of claim 4 comprising 12 percent of aluminum, 65 percent of HMX oxidizer and 19.2 percent of said polymer.

6. The composite type propellant of claim 4 comprising 25 percent of said polymer, 50 percent of ammonium perchlorate oxidizer, and 25 percent of aluminum fuel.

7. The composite type propellant of claim 4 comprising 20 percent of said polymer, 15 percent of aluminum fuel, and 65 percent of HMX oxidizer.

8. The composite type polymer of claim 4 wherein said polymer is cured with a difunctional isocyanate.

9. The composite type polymer of claim 4 wherein the molecular weight of said polymer varies from about 750 to about 3,000.

10. A solid propellant composition according to claim 1 wherein said composition is a double-base type propellant containing said polymer, nitrocellulose, and a high energy explosive selected from the group consisting of nitroglycerin, diethylene glycol dinitrate, and methyl trimethylolmethane trinitrate.

11. The double-base type propellant of claim 10 comprising from about 30 to about 50 percent by weight of said high energy explosive, from about 10 to about 59 percent by weight of nitrocellulose and from about 1 to about 30 percent by weight of said polymer such that the amount of said polymer is equal to or less than the amount of nitrocellulose present.

12. The composite type composition of claim 11 wherein said polymer is cured with a difunctional isocyanate.

13. The composite type composition of claim 11 wherein the molecular weight of said polymer varies from about 1,000 to about 2,500.