PROPELLANT COMPRISING NITROCELLULOSE, NH₄NO₃, RUBBERY POLYMERS AND BURNING RATE MODIFIERS

FIG. 1
EFFECT OF BORON AND ALUMINUM ON THE BURNING RATE OF AN AMMONIUM NITRATE POLYMER PROPELLANT

FIG. 2
THE EFFECT OF BORON ON THE BURNING RATE OF AN AMMONIUM NITRATE SINGLE-BASE PROPELLANT
May 20, 1969

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PROPELLANT COMPRISING NITROCELLULOSE, NH₄NO₃, RUBBERY POLYMERS AND BURNING RATE MODIFIERS

Filed March 18, 1963

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FIG. 3
EFFECT OF BORON ON THE BURNING RATE OF A SINGLE BASE AMMONIUM NITRATE PROPELLANT

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>IF235</th>
<th>IF167</th>
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<tbody>
<tr>
<td>INGREDIENTS</td>
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<tr>
<td>NITROCELLULOSE</td>
<td>20.0 20.0</td>
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</tr>
<tr>
<td>AMMIONIUM NITRATE</td>
<td>45.0 60.0</td>
<td></td>
</tr>
<tr>
<td>ETHYL CENTRALITE</td>
<td>0.6 0.5</td>
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<tr>
<td>BORON</td>
<td>13.9 2.0 ADDED</td>
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<tr>
<td>METHYL METHACRYLATE</td>
<td>15.0 13.5</td>
<td></td>
</tr>
<tr>
<td>ACRYLONITRILE</td>
<td>5.0 5.0</td>
<td></td>
</tr>
<tr>
<td>LUPERSOL DDM</td>
<td>0.5 0.5</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 4
EFFECT OF AMMONIUM NITRATE CONTENT ON THE BURNING RATE OF AN AMMONIUM NITRATE SINGLE-BASE PROPELLANT

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FIG. 5
BURNING-RATE CURVES FOR AMMONIUM NITRATE PROPELLANTS BASED ON PENTAERYTHRITOLTRINITRATE ACRYLATE-2-NITROETHYL METHACRYLATE

FIG. 6
COMPARISON OF THE CATALYTIC EFFECT OF BORON AND TITANIUM DIOXIDE ON AN AMMONIUM NITRATE POLYMER PROPellant
This invention relates to solid rocket propellant compositions. Specifically, this invention is concerned with the use of certain additives to alter the burning rate of solid propellant compositions containing ammonium nitrate. One problem which exists in the area of solid propellants is the manner in which the burning rate is affected by the initial temperature of the propellant grain and the pressure of the combustion chamber. The relationship of the propellant burning rate to initial grain temperature and chamber pressure is illustrated by the following equation:

\[ r = a p n \]

The burning rate, \( r \), is usually expressed in inches per second while the chamber pressure, \( p_n \), is expressed in pounds per square inch. The variable, \( a \), is a constant which is dependent upon the initial grain temperature. The exponent, \( n \), is a constant for a given propellant composition and is usually referred to as the burning rate exponent. For practical application, the value of \( n \) should be between zero and one, preferably as close to zero as possible. The closer the value of \( n \) approaches one, the more sensitive the burning rate to the chamber pressure.

Generally, for a particular solid propellant, a graph of the logarithm of \( r \) plotted against \( n \) (logarithm \( p_n \)) plus the logarithm of \( a \) is straight line. As the slope of this line approaches zero, the less sensitive is the particular propellant composition to the chamber pressure. For most applications it is desirable that the burning rate of the propellant be relatively insensitive to the pressure of the combustion chamber.

It is possible to alter the burning rates of various solid propellants by incorporating in the propellant compositions certain additives. For certain pressure ranges, the propellant compositions, incorporating these additives, burn at a fairly uniform rate. This effect is normally referred to as mesa or plateau effect. (See U.S. Patent 2,982,638 to Cooley et al.) The particular range of pressure in which the burning rate of the propellant is fairly constant is also known as the region of low slope.

It has now been determined that solid propellant compositions containing ammonium nitrate as an oxidizer will exhibit regions of low slope if there is incorporated in the composition an additive selected from the group of boron, mixtures of boron and aluminum, titanium dioxide, and antimony. The regions of low slope brought about by these additives occur within the pressure range of 4,000 p.s.i. to 16,000 p.s.i. Since chamber pressures of 8,000 p.s.i. to 10,000 p.s.i. are encountered in smaller rockets such as anti-tank rockets and artillery rockets, the rocket propellants of the invention are particularly suitable for application in this area.

In accordance with the foregoing, it is an object of this invention to provide a method of altering the burning rates of solid rocket propellants containing ammonium nitrate.

A further object of the invention is to provide a method of creating plateaus or areas of low slope in the burning rate of solid propellant compositions containing ammonium nitrate.

Another object of the present invention is to provide solid propellant compositions containing ammonium nitrate and certain additives which modify the burning rate of said composition.

A still further object of the instant invention is to provide solid propellant compositions which contain ammonium nitrate and whose burning rate is relatively insensitive to an increase of pressure in the combustion chamber within certain pressure ranges.

An additional object of the invention is to provide solid propellant compositions containing ammonium nitrate which exhibit regions of low slope in their burning rates. The manner in which these and other objects may be accomplished will become apparent from the detailed description presented hereinbelow.

FIGURE 1 is a graph comparing the burning rate modifying effect of a boron catalyzed propellant composition with the burning rates of two other compositions not containing a catalyst.

FIGURE 2 graphically illustrates the plateau effect achieved in the burning rate of two propellant compositions modified according to the invention and the total absence of this effect in a similar unmodified propellant composition.

FIGURE 3 depicts the effect on the burning rate plateau using various amounts of boron as the burning rate modifier.

FIGURE 4 graphically illustrates the effect on the burning rate plateau when the amount of ammonium nitrate in the composition is varied.

FIGURE 5 is a graph showing the plateau effect achieved in a solid propellant composition which incorporates the copolymer of pentaerythritol trinitrate acrylate and 2-nitroethyl methacrylate; and

FIGURE 6 graphically compares the plateau effect achieved in the burning rate of propellant compositions using boron on titanium dioxide as the modifier. Many solid propellant compositions employ ammonium nitrate as an oxidizer. (See U.S. Patent 3,051,347 to Phillipson and U.S. Patent 3,005,672 to Adelman.) As mentioned above, it has now been determined that the burning rate of these solid propellant compositions containing ammonium nitrate can be modified by incorporating in the composition a burning rate modifier selected from the group consisting of boron, titanium dioxide, antimony, and mixtures of boron and aluminum. The effect of these modifiers is to create regions of low slope in the burning rate as shown in FIGURES 1 through 6. Boron is the preferred member of this group of burning rate modifiers.

The method for altering the burning rate of solid propellant compositions containing ammonium nitrate according to the invention is simple. All that is required to induce a region of low slope in the burning rate is to thoroughly mix one or more of the previously identified burning rate modifiers with the other ingredients of the composition prior to curing. The amount of modifier to be added depends on the particular modifier selected as explained later herein.

The burning rate modifiers of the invention are selective in their ability to induce regions of low slope in propellant burning rates. Only those propellant compositions which employ ammonium nitrate as the oxidizer achieve the mesa or plateau effect in their burning rates. Accordingly, for the catalyst of this invention to be effective for the purpose for which they are intended, ammonium nitrate should constitute the major portion of the oxidizer for the propellant composition. Preferably, ammonium nitrate should be the only oxidizer employed.

The catalyst will effectively catalyze the burning rate of any conventional propellant employing ammonium nitrate.
nitrate as the oxidizer. However, for practical reasons based on their intended use in smaller military rockets, the compositions in which the catalysts are employed usually comprise nitrocellulose and a polymeric binder in addition to the ammonium nitrate. Compositions of this type are readily extended into grains which perform very satisfactorily in small rocket motors. However, to demonstrate the ability of the burning rate catalyst of the invention to induce a plateau effect in the burning rates of propellant compositions totally different from those using nitrocellulose, a composition was prepared comprising ammonium nitrate, pentachlorothiol trinitrate acrylate, 2-nitroacetetyl methacrylate, and boron. Upon ignition and burning, this composition demonstrated a region of low slopes between about 4,000 p.s.i. and 7,000 p.s.i. as graphically illustrated in FIGURE 1.

As previously mentioned, the amount of burning rate modifier to be added to the compositions depends upon the particular catalyst added to the composition. For example, substituting 2% by weight anthracene for the boron in the composition of FIGURE 1 produces a low slope region between 6,000 p.s.i. and 8,000 p.s.i. If the amount of anthracene is increased to 4% by weight, the region of low slope extends from 6,000 p.s.i. to 10,000 p.s.i. However, in addition of 6% by weight anthracene resulted in no low slope region in the burning rate. In the same manner, substitution of 2% by weight of titanium dioxide or a 4% by weight mixture of equal weights of aluminum and boron for the boron in the composition of FIGURE 1 also induces regions of low slope in the range of 6,000 p.s.i. to 10,000 p.s.i. FIGURE 6 compares graphically the catalytic effect of boron and titanium dioxide.

It is interesting to note that aluminum, next above boron in the periodic group, increases the propellant burning rate but does not produce a plateau effect as shown by FIGURE 1.

Since boron is the preferred burning rate modifier, it will be discussed separately. Boron produces a region of low slope in the burning rate of propellant compositions when it is present in the composition in an amount from about 1.9% by weight to 15% by weight. The actual plateau region produced in the burning rates of boron catalyzed compositions containing about 1.9% by weight boron and 13.9% by weight boron are illustrated in FIGURE 3. Adding 4% by weight boron to a propellant composition produces a region of low slope over the same pressure range as 2% by weight boron but gives a slightly increased burning rate of approximately 0.70 in./sec. For most applications, from 1.9% to about 4% by weight boron is preferred.

Despite its large specific surface, boron does not inhibit polymerization of the binder. This is in marked contrast to carbon black of similar specific surface which completely inhibits polymerization in amounts greater than 3% by weight.

The boron utilized in the examples disclosed herein was composed of particles which averaged 1 micron in size. As far as is practical, it is best to employ smaller sizes of a given burning rate modifier since better dispersion is usually achieved.

The nitrocellulose employed in the examples described herein contained 13.25% by weight nitrogen. However, any nitrocellulose containing at least 12.5% by weight nitrogen can be utilized.

The nitrocellulose content of the composition can vary in the range of 15% to 35% by weight. Best performance was achieved with boron compositions wherein nitrocellulose comprised about 20% by weight of the total composition.

To further study the effect of the nitrocellulose on the burning rate, three compositions were prepared consisting of only ammonium nitrate, nitrocellulose, and ethyl Centralite. The actual ratio of ingredients in these compositions is shown in Table I below.

<table>
<thead>
<tr>
<th>Ingredient No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium nitrate</td>
<td>30</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Nitrocellulose (U.S.P. No.)</td>
<td>60</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>Ethyl Centralite</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Boron (added)</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

After extrusion into grains each of the compositions was tested to determine its burning rate and the effect of the boron catalyst. In each case the propellant burning rate exhibited a region of low slope from 6,000 p.s.i. to 12,000 p.s.i. Compositions which contained over 50% nitrocellulose were unsatisfactory.

Ammonium nitrate variations in the propellant compositions resulted in lowering the burning rate within the region of low slope. For example, when the amount of ammonium nitrate in the composition shown in FIGURE 4 was decreased from 60% to 50% by weight the average burning rate within the plateau was reduced from about 0.60 in./sec. to 0.48 in./sec. Similarly, increasing the ammonium nitrate content from 20% to 21.5% by weight produces a corresponding increase in the burning rate within the plateau as shown in FIGURE 2. Operable propellant compositions which can be effectively catalyzed by the burning rate modifier of the invention contain from 45% to 65% by weight ammonium nitrate.

The propellant composition of IF167 shown in FIGURE 1 was modified by the substitution of methyl, ethyl, and butyl acrylate for methyl methacrylate. There were no difficulties in processing and extending the resulting propellant compositions. As the length of the alcohol portion of the ester increased the propellant became increasingly flexible. The ballistic properties and the region of low slope in this series of propellants remained essentially unchanged.

It will be obvious to those skilled in the art that other polymeric binders can be substituted for the copolymer of acrylonitrile and methyl methacrylate utilized in the compositions shown in FIGURES 1, 2, 3, 4, and 6. In addition to the use of the alkyl esters of acrylic acid referred to hereinabove, other alkyl esters of methacrylic acid such as butyl methacrylate can be employed. The polymers of the diolefins as exemplified by 1,3-butadiene, isoprene, methylpentadiene, and chloroprene can be utilized. Moreover, the copolymers of these diolefins with each other are also satisfactory binder compositions. Acrylic and methacrylic acid are suitable in lieu of acrylonitrile and in some cases to be preferred. There are many other polymeric binders well known in the propellant art which can be employed in the compositions of the invention. The essential feature, as previously explained, is that the composition employ ammonium nitrate as the oxidizer.

The amount of polymeric binder in the compositions can vary from 15% to 50% by weight. In addition to its role as a binder, the polymer also acts as a fuel in the composition. Thus, the optimum amount of binder depends upon the amount of available oxygen to burn the binder as well as the desired physical properties.

The copolymers of acrylonitrile and an ester of the formula

\[
\text{RCH} = \text{C} = \text{CH} - \text{COO} - \text{R'}
\]

wherein R is hydrogen or methyl and R' is a lower alkyl group of up to four carbon atoms are particularly useful as binders in the propellant compositions of the invention and are thus preferred. Examples of R' include methyl, ethyl, propyl, butyl, and isobutyl groups.

Depending on the type of binder employed, it may be necessary to include small amounts of additional materials in the composition to initiate polymerization. For
example, the commercially available peroxides such as Lupersol DDM assist in initiating the polymerization of most of the compositions shown in the figures. Ethyl Centralite, or some other stabilizer, is employed in compositions containing nitrocellulose to prevent decomposition. Some compositions, such as that shown in FIGURE 5, do not require any additives. The means for curing the composition depend on the binder employed. However, since the use of these binders is old, the means for effecting a cure are well known.

The preferred compositions of the invention are the boron catalyzed compositions containing nitrocellulose as exemplified in FIGURES 1, 2, 3, 4, and 6. The following example demonstrates the preparation of such compositions.

**Example**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Actual weight</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose (15.29% N)</td>
<td>75.0</td>
<td>25</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>21.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>47.3</td>
<td>12.5</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>19.2</td>
<td>5.5</td>
</tr>
<tr>
<td>Ethyl Centralite</td>
<td>1.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Lupersol DDM</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Boron</td>
<td>7.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

1 Added.

The ingredients were thoroughly mixed with a sigma blade mixer for 80 minutes at room temperature and then extruded into grains of the desired weight size. The composition was cured by the initiating action of the Lupersol DDM (peroxide) and heating at 50° C. for 24 hours. Until polymerization, the acrylonitrile and methyl methacrylate serve as solvents.

The size of the extruded grain will depend upon the particular rocket motor in which the grain is to be employed.

To further clarify the discussion of the invention, it is pointed out that sometimes the burning rate modifiers are spoken of as being added to the composition whereas in other instances the modifiers are said to comprise a certain portion of the composition. It should be apparent to those skilled in the art that, for example, 2% by weight boron is added to a composition then the boron comprises 1.96% by weight of the total composition.

The above description is for the purpose of illustration and clarification and no undue limitations should be imposed upon the present invention as a result thereof except as set forth in the appended claims.

We claim:

1. A solid propellant composition comprising a cured intimate mixture of from 15% to 35% by weight nitrocellulose; 45% to 65% by weight ammonium nitrate; 15% to 30% by weight of a rubbery polymer, and from 1.9% to 13% by weight boron.

2. A solid propellant composition comprising a cured mixture of from 15% to 35% by weight nitrocellulose, 45% to 65% by weight ammonium nitrate, 15% to 50% by weight of a rubbery polymer, and from 1.9% to 4% by weight antimony.

3. A solid propellant composition comprising a cured intimate mixture of from 15% to 35% by weight nitrocellulose, 45% to 65% by weight ammonium nitrate, 15% to 30% by weight of a rubbery polymer, and from 1.9% to 4% by weight titanium dioxide.

4. A solid propellant composition comprising a cured intimate mixture of from 15% to 35% by weight nitrocellulose, 45% to 65% by weight ammonium nitrate, 15% to 50% by weight of a rubbery polymer, and from 1.9% to 4% by weight of a mixture consisting essentially of equal parts by weight of boron and aluminum.

5. A solid propellant composition comprising a cured intimate mixture of from 15% to 35% by weight nitrocellulose; 45% to 65% by weight ammonium nitrate; 15% to 50% by weight of a rubbery polymer selected from the group consisting of copolymers of acrylonitrile and an ester of the formula:

\[
\text{H}_2\text{O} \rightarrow \text{O} \rightarrow \text{C}\text{H}=\text{C} \rightarrow \text{O} \rightarrow \text{O} \rightarrow \text{BR}
\]

wherein R is selected from the group consisting of hydrogen and methyl and R' is lower alkyl of 1–4 carbon atoms and copolymers of pentaerythritol trinitrate acrylate and 2-nitroethoxy methyl acrylate; and 1.9% to 15% by weight of boron.

6. A composition according to claim 5 wherein said rubbery polymer is the copolymer of acrylonitrile and methyl methacrylate and said boron is present in an amount of about 2% by weight.

7. A solid propellant composition consisting essentially of a cured intimate mixture of about 19.6% by weight nitrocellulose, about 58.8% by weight ammonium nitrate, about 19.6% by weight of the copolymer of methyl methacrylate and acrylonitrile, and about 1.9% by weight boron.

8. A solid propellant composition consisting essentially of a cured intimate mixture of about 47% by weight ammonium nitrate, about 28.5% by weight pentaerythritol trinitrate, about 20.5% by weight 2-nitroethoxy methyl acrylate, and about 1.9% by weight boron.

9. In solid propellant compositions comprising an intimately cured mixture of from 15% to 35% by weight nitrocellulose, 45% to 65% by weight ammonium nitrate, and 15% to 50% of a rubbery polymer, the method of modifying the burning rate thereof by adding to said composition before curing a member selected from the group consisting of 2% to 15% by weight boron, 2% to 4% by weight antimony, 2% to 4% by weight titanium dioxide, and 2% to 4% by weight of a mixture consisting essentially of equal parts by weight of aluminum and boron.

10. In solid propellant compositions comprising an intimate mixture of from 15% to 35% by weight nitrocellulose, 45% to 65% by weight ammonium nitrate, and 15% to 50% by weight of a rubbery polymer selected from the group consisting of copolymers of acrylonitrile and an ester of the formula:

\[
\text{H}_2\text{O} \rightarrow \text{O} \rightarrow \text{C}\text{H}=\text{C} \rightarrow \text{O} \rightarrow \text{O} \rightarrow \text{BR}
\]

wherein R is selected from the group consisting of hydrogen and methyl and R' is lower alkyl of 1–4 carbon atoms, and copolymers of pentaerythritol trinitrate acrylate and 2-nitroethoxy methyl methacrylate; the method of modifying the burning rate thereof by adding to said composition before curing 2% to 16% by weight boron.

11. The method according to claim 9 wherein said rubbery polymer is the copolymer of methyl methacrylate and acrylonitrile and said boron is added in an amount of about 2% by weight.

References Cited

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Date</th>
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<th>Description</th>
</tr>
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<tr>
<td>3,196,059</td>
<td>7/1965</td>
<td>Godfrey</td>
<td>149—19</td>
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<tr>
<td>3,203,773</td>
<td>8/1965</td>
<td>Landesman</td>
<td>149—22 X</td>
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LELAND A. SEBASTIAN, Primary Examiner.

U.S. Cl. X.R.

149—20, 22, 38, 41, 44, 49, 50, 60, 88, 100