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SOLID COMPOSITE PROPELLANTS CONTAINING BURNING RATE CATALYSTS

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This invention relates to solid propellant compositions. More particularly, the invention relates to solid propellant compositions having higher burning rate characteristics.

Recently great emphasis has been placed on the development of solid propellant compositions for use in the propulsion of rockets, such as ground-to-ground missiles, ship-to-shore missiles, air-to-air missiles and air-to-ground missiles. A suitable solid propellant material has been obtained by compressing a solid oxidant such as ammonium nitrate or ammonium perchlorate in a binder component which is present in sufficient amount to form a continuous matrix around the oxidant. Depending upon the type of binder employed and the method of curing, a propellant could be made wherein it exhibited good mechanical properties such as high elongation and tensile strength in addition to being non-brittle and resistant to cracking or fissuring when subjected to temperature cycling. However, in many solid propellant applications, higher buring rates are desirable than are presently available in conventional propellants to obtain maximum efficiency.

One approach to obtaining an increased burning rate of these solid propellant compositions involved increasing the concentration of the oxidant component to near its stoichiometric ratio with the binder component. However, at high concentrations of oxidant component the amount of the binder component present approaches the amount insufficient to form a continuous matrix in which to disperse the oxidant component whereby the mixture burns at explosive rates.

Another approach under the prior art directed to increasing the burning rate of solid propellants was to incorporate a powdered metal with the oxidant of the composition to catalyze its oxidation. The powdered metal particles alone, such as aluminum metal, burn in air at a temperature of around 3500° C. and produce an intense heat. However, it has been observed that use of aluminum metal reduced or had no effect on the burning rate of a propellant, hence its use was disadvantageous. Even where increases have occurred, the present fuel mixtures though using only small amounts or organoboranes and boron hydrides to the compositions have been found to increase the burning rate of solid propellant compositions 4–5 times over those compositions employing metallic flakes as burning catalysts. This dramatic and unexpected result will be described in more detail in the examples hereinafter described.

An object of this invention is to provide a composition useful as fuel which is adapted to burn at a non-explosive rate and produce a large amount of gases.

Another object of this invention is to provide an improved propellant composition.

Yet another object of this invention is to provide a solid fuel propellant composition which burns at a reproducible rate of 4 and 5 times faster than the solid fuel propellant compositions heretofore known under the prior art.

A still further object of this invention is to provide a propellant composition having a burning rate of 1.75 inches per second at a 1000 lbs. per square inch and 70° F.

Other objects and advantages of the invention will be

apparent to those skilled in the art in view of this disclosure.

The composition of this invention consists, on a weight basis of:

(1) About 12% to about 26% of a rubbery polymer selected from the class consisting of hydrocarbons comprising polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, and polyurethanes comprising a fully saturated polybutylene oxide liquid polymer, having a viscosity of 14,000–19,000 centistokes at 25° C. and containing 4.0%±.3% isocyanate groups by weight; a liquid polyester having a viscosity of 80,000 ±15,000 centistokes at 25° C. and containing 5.9±0.5% by weight of isocyanate end groups; fully saturated polypropylene glycol liquid polymers, having a viscosity of 14,000 to 19,000 centistokes at 25° C. and containing 3.2±0.4% isocyanate groups by weight and a polybutadiene liquid polymer containing 1.6% by weight of carboxy groups and having a molecular weight of 55,000 at a viscosity of 59,000 centistokes at 25° C.

(2) About 2% to about 10% of a burning rate catalyst selected from the group comprising decaborane; [1] HEF-3; isopropenylcaborane and ferrocene.

(3) With the remainder essentially a solid inorganic oxidizing salt as an oxidant component.

The amount of binder in the composition may vary, on a weight basis, from about 12% to about 26%. Variation within this range being made to obtain stoichiometric balance with respect to oxygen content of the composition for improved operation.

The effects of the organoboranes were evaluated on two distinct propellant binder systems:

(1) Hydrocarbon binder (polyisobutylene).

(2) A polyurethane binder consisting of one member selected from the group consisting of a liquid polyester containing 5.9±0.5% by weight of isocyanate end groups and having a viscosity of 80,000±15,000 centistokes at 25° C., and a saturated polybutylene oxide liquid polymer containing 4.0±0.3% isocyanate groups by weight and having a viscosity of 14,000–19,000 centistokes at 25° C.

The following solid propellant compositions demonstrate that when made in accordance with the teaching of this invention their burning rates in both the hydrocarbon and polyurethane binder systems are greatly accelerated over all known ballistic additives for them and all other known propellant systems. The addition of organoboranes and boron hydrides unexpectedly produced a marked and dramatic increase in the burning rates.

The burning rates were tested in a Crawford Bomb. Burning rate test strips of the gas-forming composition are prepared by extruding or molding at a temperature below about 120° C. under pressure (amount of pressure immaterial). The strands are coated with lacquer grade cellulose acetate on the sides to give strands which burn like a cigarette and then are burned in a pressure bomb under nitrogen pressure. Four to six strands ¼" x ¼" and 5" in length are burned at varying pressures between 600 and 1800 p.s.i. Plotting burning rate in inches per second against pressure on log—log paper gives a straight line. The slope of this straight line is defined as the exponent of the burning rate related to pressure in the formula

$$B=\gamma\left(\frac{P}{1000}\right)^n$$

where B is the linear burning rate at pressure "p," γ is the linear burning rate for the composition at 1000 p.s.i. "p" is pressure in p.s.i. in the burning chamber and "n" is the

[1] HEF-3 is a mixture of alkyl-decaboranes consisting on a weight basis of 67% monoethyldecaborane, 26% diethyldecaborane, 2.5% triethyldecaborane and 4.5% decaborane.

pressure exponent showing dependence of the burning rate on pressure. A pressure exponent less than about 0.8 and preferably less than about 0.7 is desirable for the ammonium nitrate and ammonium perchlorate propellant compositions.

EXAMPLE I

Ingredient:	Weight percent
Oxidant, ammonium perchlorate	73
Binder, polyisobutylene	25
Catalyst, decaborane	2

This composition was tested in a Crawford Bomb Apparatus and demonstrated a burning rate of 0.56 inch/second at 1000 p.s.i. and 70° F.

Under the same conditions, a control composition consisting of 74% ammonium perchlorate and 26% polyisobutylene showed a burning rate of 0.45 inch/second. The addition of 2% decaborane increased the burning rate 25%. The pressure exponent (450–1600 p.s.i.) was 0.59 for the control and 0.56 for the composition.

EXAMPLE II

A second composition containing the same components as the composition of Example I, but in different proportions was prepared. The finished composition consisted of the following:

Ingredient:	Weight percent
Oxidant, ammonium perchlorate	74
Binder, polyisobutylene	21
Catalyst, HEF-3	5

This composition burned at a rate of 1.05 inch/second at 1000 p.s.i. and 70° F. This represented an increase in the burning rate of 133% over the control. The pressure exponent (450–1600 p.s.i.) was 0.58.

EXAMPLE III

A composition was prepared according to the following formula

Ingredient:	Weight percent
Oxidant, ammonium perchlorate	74
Binder, polyisobutylene	21
Catalyst, HEF–3	5

When tested in a Crawford Bomb, this composition burned at a rate of 1.11 inch/second at 1000 p.s.i. and 70° F. This represented an increase of 147% in the burning rate over the control composition. A pressure exponent (450–1600 p.s.i.) of 0.62 was obtained.

EXAMPLE IV

Ingredient:	Weight percent
Oxidant, ammonium perchlorate	75
Binder, a liquid polyester containing 5.9±0.5% by weight of isocyanate end groups and having a viscosity of 80,000±15,000 centistokes at 25° C.	20
Catalyst, HEF-3	5

This composition burned at a rate of 1.25 inches per second at 70° F. This represented an increase of 290% in the burning rate when compared with the control. The control containing 75% by weight of ammonium perchlorate and 25% by weight of a liquid polyester containing 5.9±0.5% by weight of isocyanate end groups and having a viscosity of 80,000±15,000 centistokes at 25° C. polymer burned at a rate of 0.32 inch per second. A pressure exponent (600–1600 p.s.i.) of 0.31 was measured for the control. The composition had a pressure exponent (800–1300 p.s.i.) of 0.59.

EXAMPLE V

Ingredient:	Weight percent
Oxidant, ammonium perchlorate	68
Binder, a fully saturated polybutylene oxide liquid polymer containing 4.0 ± 0.3% isocyanate groups by weight and having a viscosity of 14,000–19,000 centistokes at 25° C	12
Catalyst:	
Isopropenylcarborane	10
Aluminum powdered metal	10

This composition burned at a rate of 0.98 inch/second under 1000 p.s.i. at 70° F. This represented an increase of 200% in the burning rate over a control containing 68% ammonium perchlorate, 10% aluminum metal and 22% a fully saturated polybutylene oxide liquid polymer containing 4.0±0.3% isocyanate groups by weight and having a viscosity of 14,000–19,000 centistokes at 25° C. material. The control burned at 0.32 inch/second. The pressure exponent (450–1000 p.s.i.) was calculated to be 0.35 for the control and 0.55 for the composition.

EXAMPLE VI

Ingredient:	Weight percent
Oxidant, ammonium perchlorate	68
Binder, a liquid polyester containing 5.9±0.5% by weight of isocyanate end groups and having a viscosity of 80,000±15,000 centistokes at 25° C.	17
Catalyst:	
Ferrocene	5
Aluminum	10

This composition had a burning rate of 0.55 inch/second at 1000 p.s.i. and 70° F. This represented an increase of 27% in the burning rate over the control. The pressure exponent (450–1000) was 0.46.

It is understood that various changes and additions in equiavlent materials may be substituted for those set forth in the above examples when compounding the fuel of this invention. The proportionate amounts of the oxidant and binder may be varied, as heretofore described; however, in order to achieve the best results the concentration of the catalyst should be kept within the limits of 2–10% by weight. Such changes and variations are deemed to be contemplated to come within the spirit and scope of this invention and which are particularly set forth in the appended claims.

What is claimed is:

1. A solid propellant composition comprising: from 12 to 26 weight percent of a binder component wherein said binder comprises one member selected from the group consisting of polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, and polyurethanes comprising a liquid polyester containing 5.9±0.5% by weight of isocyanate end groups and having a viscosity of 80,000±15,000 centistokes at 25° C., a fully saturated polybutylene oxide liquid polymer containing 4.0±0.3% isocyanate groups by weight and having a viscosity of 14,000–19,000 centistokes at 25° C., fully saturated polypropylene glycol liquid polymers containing 3.2±0.4% isocyanate groups by weight and having a viscosity of 14,000–19,000 centistokes at 25° C. and a polybutadiene liquid polymer containing 1.6% by weight of carboxy groups and having a molecular weight of 55,000 and a viscosity of 59,000 centistokes at 25° C; 2 to 10 weight percent of a catalyst for increasing the burning rate of the said propellant composition wherein said catalyst is selected from the group consisting of decaborane; a mixture of alkyl-decaborances consisting on a weight basis of 67% monoethyldecaborane, 26% diethyldecaborane, 2.5% triethyldecaborane and 4.5% decaborane; isopropenylcarborane and ferrocene; and the balance being an oxidant component of a solid inorganic oxidizing salt.

2. A solid propellant of the character described in claim 1, comprising the following mixture in parts by weight:

	Percent
Ammonium perchlorate	73
Polyisobutylene	25
Decaborane	2

3. A solid propellant of the character described in claim 1, comprising the following mixture in parts by weight:

	Percent
Ammonium perchlorate	74
Polyisobutylene	21
A mixture of alkyl-decaborances consisting on a weight basis of 67% monoethyldecaborane, 26% diethyldecaborane, 2.5% triethyldecaborane and 4.5% decaborane	5

4. A solid propellant of the character described in claim 1, comprising the following mixture in parts by weight:

	Percent
Ammonium perchlorate	75
A liquid polyester containing 5.9±0.5% by weight of isocyanate end groups and having a viscosity of 80,000±15,000 centistokes at 25° C.	20
A mixture of alkyl-decaborances consisting on a weight basis of 67% monoethyldecaborane, 26% diethyldecaborane, 2.5% triethyldecaborane and 4.5% decaborane	5

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