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Blackwell

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[54] **SOLID PROPELLANT COMPOSITION**

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[58] **Field of Search** 52/0.5; 149/19, 20, 149/36

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EXEMPLARY CLAIM

1. A solid propellant composition comprising: from 60 to 90 weight per cent of an oxidizer component selected from the group of solid inorganic oxidizing salts consisting of ammonium perchlorate, the alkali metal perchlorates, ammonium nitrate, the alkali metal nitrates, and mixtures thereof, at least a major portion of said oxidizer component being at least one of said perchlorates; from 10 to 40 weight per cent of a binder component comprised of a rubbery material selected from the group consisting of natural rubber, synthetic rubber polymers, and mixtures thereof; and from 0.1 to 8 weight per cent of a burning rate depressing agent selected from the group consisting of ammonium fluoborate, hydrazine dihydrochloride, barium periodate, and ferric oxalate.

19 Claims, No Drawings

SOLID PROPELLANT COMPOSITION

This invention relates to solid propellant compositions. In another aspect this invention relates to solid propellant compositions containing a burning rate depressing agent.

Solid propellants can be classified with respect to composition as double base type, single base type, and composite type. An example of a double base propellant is "ballistite" which comprises essentially nitroglycerine and nitrocellulose. Examples of single base propellants are nitrocellulose and trinitrotoluene. Composite type propellants are generally composed of an oxidizer, and a binder or fuel. Said composite type propellants may contain other materials to facilitate manufacture or increase ballistic performance such as a burning rate catalyst.

Rocket propellants have achieved considerable commercial importance as well as military importance. Jet propulsion motors of the type in which the propellants of this invention are applicable can be employed to aid a heavily loaded plane in take-off. Said motors can also be employed as an auxiliary to the conventional power plant when an extra surge of power is required. Said motors can also be employed to propel projectiles and land vehicles. Said propellants can also be used for uses other than propulsion. For example, they can be used as gas generators in starting devices, power units where a fluid is employed as a motive force, and other applications where a comparatively large volume of gas is required in a relatively short period of time.

Recently, it has been discovered that superior solid propellant materials are obtained comprising a solid oxidant such as ammonium nitriate or ammonium perchlorate, and a rubbery material such as a copolymer of butadiene and a vinylpyridine or other substituted heterocyclic nitrogen base compound, which after incorporation is cured by a quaternization reaction or a vulcanization reaction. Solid propellant mixtures of this nature and a process for their production are disclosed and claimed in copending application, Ser. No. 284,447, filed Apr. 25, 1952, by W. B. Reynolds and J. E. Pritchard, now U.S. Pat. No. 3,003,861 issued Oct. 10, 1961

In the utilization of solid propellant compositions, it is important to control the burning rate and thus be able to control the amount of thrust developed per unit of time for a given charge of propellant. In many instances, burning rate catalysts are utilized to increase the burning rate. However, with some oxidizers, e.g., ammonium perchlorate, it is desirable in many instances to decrease the burning rate. It frequently happens that composite solid propellants utilizing ammonium perchlorate as the major portion of the oxidizer component are satisfactory from the standpoint of other performance characteristics, such as specific impulse, but possess too high a burning rate.

One of the most important solid propellant parameters is the burning rate of the propellant. The basic solid propellant burning equation for restricted solid propellants, such as the type with which this invention is concerned, is expressed as:

$r = k\ (p_c)^n$ where r is the burning rate in inches per second; p_c is the combustion chamber pressure in pounds per square inch; k is a constant which varies with the ambient grain temperature; and n is a constant known as the burning rate exponent.

Inspection of the above burning equation reveals that the sensitivity of the burning rate of the solid propellant to pressure is represented by the burning rate exponent n. For stable and practical operation, n should lie between 0 and 1, and preferably should be as low as possible since as n approaches 1 the burning rate is very sensitive to changes in combustion chamber pressure, and vice versa. The importance of the burning rate cannot be overestimated since the velocity at which a solid propellant is consumed during operation is determined to a great extent by the burning rate; where high thrusts are required in relatively short periods of time, solid propellants having fast burning rates are utilized. With the availability of solid propellant compositions having controllable burning rates which are relatively fast and insensitive to combustion chamber pressure, the fabricator of solid propellants has greater latitude in choosing the desired propellant grain design or charge geometry.

I have discovered that the burning rate and said burning rate exponent n of composite type propellants utilizing ammonium perchlorate or an alkali metal perchlorate as at least a major portion of the oxidizer component can be decreased by incorporating therein a small but effective amount of a burning rate depressing agent selected from the group consisting of ammonium fluoborate, hydrazine dihydrochloride, barium periodiate, and ferric oxalate. Thus, broadly speaking, the present invention resides in a solid propellant composition comprising an oxidizer component, a binder component, and said burning rate depressing agent.

An object of this invention is to provide an improved solid propellant composition. Another object of this invention is to provide a burning rate depressing agent for composite type propellants. Another object of this invention is to provide a burning rate depressing agents for composite type propellants which also serve to reduce the pressure sensitivity of said burning rate. Another object of this invention is to provide an improved propellant composition containing ammonium perchlorate or an alkali metal perchlorate as the major portion of the oxidizer component and having incorporated therein a burning rate depressing agent selected from the group consisting of ammonium fluoborate, hydrazine dihydrochloride, barium periodiate, and ferric oxalate. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

Thus, according to the invention there is provided a solid propellant composition comprising: an oxidizer component selected from the group of solid inorganic oxidizing salts consisting of ammonium perchlorate, the alkali metal perchlorates, ammonium nitrate, the alkali metal nitrates, and mixtures thereof, at least a major portion of said oxidizer component being at least one of said perchlorates; a binder component comprised of a rubbery material; and from 0.1 to 8 weight percent of a burning rate depressing agent selected from the group consisting of ammonium fluoborate, hydrazine dihydrochloride, barium periodate, and ferric oxalate.

The amount of said burning rate depressants utilized in the practice of the invention is usually within the range of 0.1 to 8 weight percent, preferably 2 to 6 weight percent of the total composition.

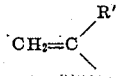
The binder component of the propellant compositions of the invention can comprise any suitable flexible rubbery material. Examples of suitable flexible rubbery materials include, among others, natural rubber, synthetic rubbery polymers, or a mixture of natural rubber and a synthetic rubbery polymer. Thus, the invention is not limited to any specific rubbery materials. Some examples of suitable rubbery polymers are polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes with comonomers such as styrene, acrylic acid, polymerizable heterocyclic nitrogen bases, and polysulfide polymers or elastomers prepared by the reaction between an aliphatic dihalide and sodium sulfide.

Said synthetic rubbery polymers can vary in consistency from liquid polymers having a viscosity of from 40 to 2000 poises, preferably 200 to 900 poises at 77° F., through very soft rubbers, i.e., materials which are soft at room temperature but will show retraction when relaxed, to those having a Mooney value (ML-4 212° F.) up to 100. Rubbery polymers having a Mooney value in the range of 5 to 50 are frequently preferred. Said polymers can be prepared by any methods known to the art.

Said copolymers of conjugated dienes with polymerizable heterocyclic bases comprises a presently preferred class of rubbery polymers for use in the binder component of the propellant of the invention. A presently preferred rubbery polymer is a copolymer of 1,3-butadiene with 2-methyl-5-vinylpyridine. One convenient method for preparing these copolymers is by emulsion polymerization at temperatures in the range between 0° and 140° F. Recipes such as the iron pyrophosphate-hydroperoxide, either sugar-free or containing sugar, the sulfoxylate, and the persulfate recipes are among those which are applicable. It is advantageous to polymerize to high conversion as the unreacted vinyl-pyridine monomer is difficult to remove by stripping.

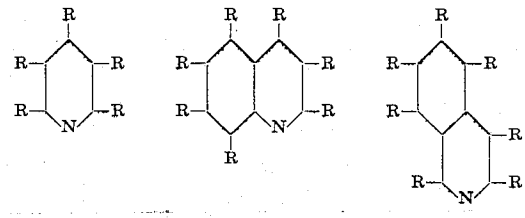
The conjugated dienes employed are those containing from 4 to 10 carbon atoms per molecule and include 1,3-butadiene, isoprene, 2-methyl-1,3-butadiene, and the like. Various alkoxy, such as methoxy, ethoxy, and cyano derivatives of these conjugated dienes, are also applicable. Thus, other dienes, such as phenylbutadiene, 2,3-dimethyl-1,3-hexadiene, 2-methoxy-3-ethylbutadiene, 2-ethoxy-3-ethyl-1,3-hexadiene, 2-cyano-1,3-butadiene, are also applicable. Instead of using a single conjugated diene, a mixture of conjugated dienes can be employed. Thus, a mixture of 1,3-butadiene and isoprene can be employed as the conjugated diene portion of the monomer system.

The polymerizable heterocyclic nitrogen bases which are applicable for the production of the polymeric materials by polymerizing said bases with a conjugated diene are those of the pyridine, quinoline, and isoquinoline series which are copolymerizable with a conjugated diene and contain one, and only one,



substituent wherein R′ is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl (isopropenyl) group. Of these, the compounds of the pyridine series are of the greatest interest commercially at present. Various substituted derivatives are also applicable but the total number of carbon atoms in the groups attached to the carbon atoms of the heterocyclic nucleus should not be greater than 15 because the polymerization rate decreases somewhat with increasing size of the alkyl group. Compounds where the alkyl substituents are methyl and/or ethyl are available commercially.

These heterocyclic nitrogen bases have the formula



where R is selected from the group consisting of hydrogen, alkyl, vinyl, alpha-methylvinyl, alkoxy, halo, hydroxy, cyano, aryloxy, aryl, and combinations of these groups such as haloalkyl, alkylaryl, hydroxyaryl, and the like; one and only one of said groups being selected from the group consisting of vinyl and alpha-methylvinyl; and the total number of carbon atoms in the nuclear substituted groups being not greater than 15. Examples of such compounds are 2-vinylpyridine; 2-vinyl-5-ethylpyridine; 2-methyl-5-vinylpyridine; 4-vinyl-pyridine; 2,3,4-trimethyl-5-vinylpyridine; 3,4,5,6-tetramethyl-2-vinylpyridine; 3-ethyl-5-vinylpyridine; 2,6-diethyl-4-vinylpyridine; 2-isopropyl-4-nonyl-5-vinylpyridine; 2-methyl-5-undecyl-3-vinylpyridine; 2,4-dimethyl-5,6-dipentyl-3-vinylpyridine; 2-decyl-5-(alpha-methylvinyl) pyridine; 2-vinyl-3-methyl-5-ethylpyridine; 2-methoxy-4-chloro-6-vinylpyridine; 3-vinyl- 5-ethoxypyridine; 2-vinyl-4,5-dichloropyridine; 2-(alpha-methylvinyl)-4-hydroxy-6-cyanopyridine; 2-vinyl-4-phenoxy-5-methylpyridine; 2-cyano-5-(alpha-methylvinyl)pyridine; 3-vinyl-5-phenylpyridine; 2-(para-methyl-phenyl)-3-vinyl-4-methylpyridine; 3-vinyl-5-(hydroxyphenyl)-pyridine; 2-vinylquinoline; 2-vinyl-4-ethylquinoline; 3vinyl-6,7-di-n-propylquinoline; 2-methyl-4-nonyl-6-vinylpyridine; 4(-alphamethylvinyl)-8-dodecylquinoline; 3-vinylisoquinoline; 1,6!-dimethyl-3-vinyliso-quinoline; 2-vinyl-4-benzylquinoline; 3-vinyl-5-chloroethylquinoline-3-vinyl-5,6-dichloriisoquinoline; 2-vinyl-6-ethoxy-7-methylquinoline; 3-vinyl-6-hydroxymethylisoquinoline; and the like.

Another preferred class of rubbery materials which can be used in the binder component of the solid propellants of the invention are the copolymers of conjugated dienes, for example 1,3-butadiene, with acrylic acid. Said copolymers are commonly prepared by emulsion polymerization at temperatures in the order of 50° C. using various monomer ratios, commonly in

the range 90/10 to 92/8 butadiene/acrylic acid. An example of a suitable recipe is

	Parts by Weight
1,3-butadiene	92
Acrylic acid	8
Water	180
Tertiary amine HCl salt [1]	5
Sulfole [2]	7

[1] Such as cetyl dimethylbenzyl ammonium chloride

[2] Tertiary dodecyl mercaptan

About one percent of phenyl-beta-naphthylamine is added to the polymers as an antioxidant. Said copolymers of 1,3-butadiene and acrylic acid are available commercially in viscosities ranging from 200–700 poises at 25° C. The liquid copolymers can be cured to solids using conventional curing agents such as the Epon curatives.

Another rubbery polymer which can be employed in the binder of the solid propellant composition of this invention is a copolymer of 1,3-butadiene with styrene. Such copolymers are commonly known in the art as GR-S rubbers. Said GR-S rubbers can be prepared by any of the well known methods employing well known recipes. Any of the well known GR-S rubbers containing from 1 to 2 and up to about 25 parts of styrene can be used in the practice of the invention. The GR-S rubber designated as 1505 is one preferred copolymer for use in the practice of the invention. GR-S 1505 can be prepared by copolymerizing 1,3-butadiene with styrene at 41° F. using a sugar free, iron activated, rosin-acid emulsified system. A charge weight ratio of butadiene to styrene is 90/10 and the polymerization is allowed to go to approximately 52 percent completion. The copolymer is then salt acid coagulated and usually has a mean raw Mooney value (ML-4) of about 40. Said copolymers usually have a bound styrene content of about 8 weight percent. Further details regarding the preparation of GR-S rubbers can be found in *Industrial and Engineering Chemistry*, 40, pages 769–777 (1948) and U.S. Pat. Nos. 2,583,277; 2,595,892; 2,609,362; 2,614,100; 2,647,109; and 2,665,269.

Another rubbery material which can be employed in the binder component of the solid propellants of the invention are the polysulfide elastomer. Said polysulfide elastomers are well known to those skilled in the art and are commonly prepared by the condensation of an aliphatic dihalide and sodium polysulfide. The dihalide is added slowly, with vigorous agitation, to an aqueous solution of sodium polysulfide. Products ranging from viscous liquids to rubber can be obtained depending upon the amount of polysulfide and dihalide used. Excess dihalide gives viscous liquids and excess polysulfide gives solid rubbers. The reaction is exothermic, requires from 2 to 6 hours, and is best carried out at about 70° C. The "rank" of the polysulfide, i.e., the value of n in Na_2S_n varies in different types of the polysulfide elastomers. Dihalides which have been used commercially are ethylene dichloride, propylene dichloride, bis(2-chloroethyl)ether, di-2-chloroethyl formal, and 1,3-glycerol dichlorhydrin. Further details regarding said polysulfide elastomers can be found in "Synthetic Rubber," G. S. Whitley, John Wiley and Sons, New York, (1954) pp 892–900.

The binder contains a rubbery material of the type hereinbefore described and, in addition, there can be present one or more reinforcing agents, plasticizers, curing agents, wetting agents, and antioxidants. Other ingredients which are employed for sulfur vulcanization include a vulcanization accelerator, a vulcanizing agent, such as sulfur, and an accelerator activator, such as zinc oxide. The finished binder usually contains various compounding ingredients. Thus, it will be understood that herein and in the claims, unless otherwise specified, the term "binder" is employed generically and includes various conventional compounding ingredients. The binder content of the propellant composition will usually range from 10 to 40 percent by weight of the total propellant composition.

The copolymer comprising a conjugated diene and a polymerizable heterocyclic nitrogen base can also be cured by a quaternization reaction by incorporating therein a quaternizing agent and subjecting the resulting mixture to quaternizing conditions of temperature. Suitable quaternizing agents include alkyl halides such as methyl iodide and methyl bromide; alkylene halides such as methylene iodide and ethylene bromide; substituted alkanes such as chloroform and bromoform; alkyl sulfates such as methyl sulfate; and various substituted aromatic compounds such as benzoyl chloride, methyl benzene sulfonate, benzotrichloride, hexachloro-p-xylene, dichloro-p-xylene, benzal chloride, and the like. The quaternizing temperature is usually in the range of 0° to 175° C., although temperatures outside this range can be used.

A general formulation for the binder component of the propellant compositions of the invention is as follows:

	Parts by Weight
Rubber	100
Reinforcing agent	0–50
Plasticizer	0–100
Wetting agent	0–10
Antioxidant	0–3
Vulcanization accelerator	0–5
Sulfur	0–2
Metal oxide	0–5
Quaternizing agent	0–25
Curing agent	0–5

Reinforcing agents which can be employed include carbon black, wood flour, lignin, and various reinforcing resins such as styrene-divinylbenzene, methyl acrylate-divinlybenzene, acrylic acid-styrene-divinylbenzene, and methyl acrylate-acrylic acid-divinylbenzene resins.

In general, any rubber plasticizer can be employed in the binder compositions. Materials such as Pentaryl A (amylbiphenyl), Paraflux (saturated polymerized hydrocarbon an organic oil supplied in different viscosity grades, described in detail on page 421 of Zimmerman and Lavine, "Handbook of Material Trade Names," 1953 edition), Circosol-2XH (petroleum hydrocarbon softener having a specific gravity of 0.940 and a Saybolt Universal viscosity at 100° F. of about 2000 seconds), di(1,4,7-trioxaundecyl) methane, ZP-211 (5,8,-11,13,16,19-hexosatricosane), and dioctyl phthalate are suitable plasticizers. Materials which provide a rubber having good low temperature properties are preferred. It is also frequently preferred that the plasticizers be oxygen-containing materials.

Wetting agents aid in deflocculating or dispersing the oxidizer. Aerosol OT (dioctyl ester of sodium sulfosuccinic acid), lecithin, and Duomeen C diacetate (the diacetate of trimethylenediamine substituted by a coconut oil product) are among the materials which are applicable.

Antioxidants which can be employed include Flexamine (physical mixture containing 65 percent of a complex diarylamine-ketone reaction product and 35 percent of N,N'-diphenyl-p-phenylenediamine), phenyl-beta-naphthylamine, 2,2-methylene-bis(4-methyl-6-tert-butylphenol), and the like. Rubber antioxidants, in general, can be employed or if desired can be omitted.

Examples of vulcanization accelerators are those of the carbamate type, such as N,N-dimethyl-S-tert-butylsulfenyl dithiocarbamate and Butyl-Eight. Butyl-Eight is a rubber accelerator of the dithiocarbamate type described in "Handbook of Material Trade Names" by Zimmerman and Lavine, 1953 Edition, as a brown liquid; specific gravity 1.01; partially soluble in water and gasoline; and soluble in acetone, alcohol, benzol, carbon disulfide and chloroform.

It is to be understood that each of the various types of compounding ingredients can be used singly or mixtures of various ingredients performing a certain function can be employed. It is sometimes preferred, for example, to use mixtures of plasticizers rather than a single material.

Oxidizers which are applicable in the solid propellant compositions of the invention are ammonium perchlorate, the alkali metal perchlorates, ammonium nitrate, and the alkali metal nitrates. As used herein, the term "alkali metal" includes sodium, potassium, lithium, cesium, and rubidium. Ammonium perchlorate is the presently preferred oxidizer. Mixtures of said oxidizers are also applicable. However, when mixtures of said oxidizers are utilized, one of said perchlorates is at least a major portion, preferably at least 75 percent by weight, of the mixture. In the preparation of the solid rocket propellant compositions, the oxidizer is ground to a particle size preferably within the range between 10 and 200 microns average particle size. The amount of oxidizer used is a major amount of the total composition and is usually within the range of about 60 to about 90 weight percent of the total propellant composition.

Finely divided high energy additives can also be included in the propellant compositions of the invention. Examples of suitable high energy additives, include, among others, the following: aluminum, boron, magnesium, iron, beryllium, lithium, alloys of aluminum, alloys of magnesium, and mixtures thereof. It is preferred that said finely divided high energy additives have a particle size less than 50 microns, more preferably less than 20 microns, and still more preferably, less than 10 microns. Said high energy additives can be used in amounts of from 0 to 16 weight percent of the base propellant. In some instances greater amounts can be used.

Thus a general formulation for the propellant compositions of the invention is as follows:

	Weight per cent
Binder	10–40
Oxidizer	60–90
Burning rate depressing agent	0.1–8
High energy additive	0–16

It is preferred that the total of the solid inorganic oxidizer and other solids such as the burning rate depressing agent and high energy additive be in the range of 70 to 87 weight percent, and the binder be in the range of 13 to 30 weight percent, of the total composition.

The various ingredients in the propellant composition can be mixed on a roll mill or an internal mixer such as a Banbury or a Baker-Perkins dispersion mixer can be employed. In the finished propellant the binder forms a continuous phase with the oxidizer being a discontinuous phase. One procedure for blending the propellant ingredients utilizes a stepwise addition of the oxidizer ingredient. The binder ingredients are first mixed to form a binder mixture and the oxidizer ingredient, having the burning rate depressant and any other solid ingredients dry blended therewith, is then added to said binder mixture in increments, usually 3 to 5, but a greater or smaller number of increments can be used if desired or necessary.

After the propellant composition has been formulated as indicated above, or by any other suitable mixing technique, rocket grains can be formed by casting, extrusion, or compression molding, utilizing techniques known to those skilled in the art.

The formulated grains are usually cured before use. The curing temperature will generally be in the range between 70° and 250° F., preferably between 150° and 250° F. The curing time must be long enough to give the required creep resistance and other mechanical properties in the propellant. Said curing time will generally range from around 2 hours, when the higher curing temperatures are employed, to 7 days when the lower curing temperatures are employed.

The following examples will serve to further illustrate the invention.

EXAMPLE I

Three cast propellant compositions having the compositions set forth in Table I below were prepared. Propellant A was a control propellant. Propellants B-1 and B-2 contained ammonium fluoborate in accordance with the invention. Said propellants were cured 48 hours at 160° F.

TABLE I

Propellant Ingredients	Weight Per Cent A	B-1[5] and B-2[6]
PBAA [1]	14.30	14.30
Epon [2]	2.85	2.85
ZP-211 [3]	2.85	2.85
Ammonium perchlorate, 18 micron	12.00	12.00
Ammonium perchlorate, 200 micron	56.00	53.80
Aluminum [4]	12.00	9.00
Ammonium fluoborate		5.20
Total	100.00	100.00

	A	B-1[5]	B-2[6]
Burning rate at 1000 psi - in./sec.	0.31	0.25	0.21
Burning rate Exponent, n	0.34	0.39	0.36

(1) Liquid copolymer of 1,3-butadiene and acrylic acid. Commercial product
(2) Epon (562), epoxide derivative of glycerol
(3) 5,8,11,13,16,19-hexosa-tricosane
(4) Aluminum R-1-511, a powdered aluminum of about 5–25 microns
(5) Ammonium fluoborate cocrystallized with the ammonium perchlorate.
(6) Ammonium fluoborate added as separate ingredient.

The above data show that the burning rates of propellants B-1 and B-2 have been decreased 19 and 32 percent respectively by including ammonium fluoborate in the propellant composition.

EXAMPLE II

Two cast propellant compositions having the compositions set forth in Table II below were prepared. Propellant C was a control. Propellant D contained hydrazine dihydrochloride in accordance with the invention. Said propellants were cured 48 hours at 160° F.

TABLE II

Propellant Ingredients – Wt.%	Weight Per Cent C	D
Bd/MVP[1], 75/25	13.37	13.37
ZP-211[2]	4.69	4.79
Dichloro-p-xylene	0.94	0.94
Kel-F Oil No. 3[3]	1.00	1.00
Ammonium perchlorate, 18 micron	12.00	12.00
Ammonium perchlorate, 200 micron	56.00	55.00
Aluminum[4]	12.00	11.00
Hydrazine dihydrochloride		2.00
Total	100.00	100.00
Burning rate at 1000 psi – in./sec.	0.46	0.33
Burning rate exponent, *n*		
to 600 psi	0.05	
600 – 1000 psi	0.43	0.17

(1) Butadiene/2-methyl-5-vinylpyridine liquid copolymer, in the ratio indicated, emulsion polymerized.
(2) 5,8,11,13,16,19-hexosa-tricosane.
(3) Liquid polymer of monochlorotrifluoroethylene.
(4) Aluminum R-1-511, a powdered aluminum of about 5–25 microns

The above data show that the burning rate and burning rate exponent were decreased 28 percent and 60 percent respectively by including hydrazine hydrochloride in the propellant composition.

EXAMPLE III

Two cast solid propellant compositions containing the ingredients set forth in Table III below were prepared. Propellant E was a control. Propellant F contained barium periodate in accordance with the invention. Said propellants were cured 48 hours at 160° F.

TABLE III

Propellant Ingredients – Wt.%	Weight Per Cent E	F
PBAA [1]	17.6	17.6
Epon 562 [2]	2.4	2.4
Ammonium perchlorate, 18 micron	12.0	12.0
Ammonium perchlorate, 200 micron	56.0	55.0
Aluminum [3]	12.0	11.0
Barium periodate		2.0
Total	100.0	100.0
Burning rate, in./sec.		
at 600 psi		0.21
at 1000 psi	0.34	0.23
Burning rate exponent, n		
300-700 psi		0.26
700-1600 psi	0.41	0.13

(1) Liquid copolymer of 1,3-butadiene and acrylic acid. Commercial product
(2) Epoxide derivative of glycerol
(3) Aluminum R-1-511, a powdered aluminum of about 5–25 microns

The above data show that the burning rate was decreased 32 percent and the burning rate exponent was decreased 68 percent by including barium periodate in the propellant composition.

EXAMPLE IV

Two cast solid propellant compositions containing the ingredients set forth in Table IV below were prepared. Propellant G was a control. Propellent H contained ferric oxalate in accordance with the invention. Said propellants were cured 48 hours at 160° F.

TABLE IV

Propellant Ingredients, Wt. %	Weight per cent G	H
PBAA[1]	17.6	17.6
Epon 562[2]	2.4	2.4
Ammonium perchlorate, 18 micron	12.0	12.0
Ammonium perchlorate, 200 micron	56.0	55.0
Aluminum[3]	12.0	11.0
Ferric oxalate		2.0
Total	100.0	100.0
Burning rate at 1000 psi – in./sec.	0.34	0.25
Burning rate exponent, *n*	0.41	0.27

(1) See Table III
(2) See Table III
(3) See Table III

The above data show that the burning rate was decrased 26 percent and the burning rate exponent *n* was decreased 34 percent by including ferric oxalate in the propellant composition.

The burning rates in the above examples were determined by forming cylindrical strands of the propellant compositions having a diameter of 3/16 inch. The cured strands were cut into strand sections approximately 7 inches long and all surfaces of said sections, except one end, were restricted to prevent burning except on said end. The strand sections were then mounted in a bomb to determine the burning rate. The bomb was maintained at a temperature of 70° F., and was pressured with nitrogen to the desired pressure. The strands were ignited, and the time required for the propellant to burn between two fusible wires spaced 5 inches apart was recorded. The burning rate in inches per second and the burning rate exponent n were computed from the results obtained.

While certain examples have been set forth above for purposes of illustration, the invention is not limited thereto. Various other modifications will be apparent to those skilled in the art in view of this disclosure. Such modifications are within the spirit and scope of the invention.

I claim:

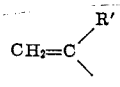
1. A solid propellant composition comprising: from 60 to 90 weight percent of an oxidizer component selected from the group of solid inorganic oxidizing salts consisting of ammonium perchlorate, the alkali metal perchlorates, ammonium nitrate, the alkali metal nitrates, and mixtures thereof, at least a major portion of said oxidizer component being at least one of said perchlorates; from 10 to 40 weight percent of a binder component comprised of a rubbery material selected from the group consisting of natural rubber, synthetic rubber polymers, and mixtures thereof; and from 0.1 to 8 weight percent of a burning rate depressing agent selected from the group consisting of ammonium fluoborate, hydrazine dihydrochloride, barium periodate, and ferric oxalate.

2. A propellant composition according to claim **1** wherein said oxidizer component is ammonium perchlorate.

3. A propellant composition according to claim **1** wherein said oxidizer component is at least about 75 weight percent ammonium perchlorate and up to about 25 weight percent ammonium nitrate.

4. A propellant composition according to claim **1** wherein said rubbery material is natural rubber.

5. A propellant composition according to claim **1** wherein said rubbery material is a copolymer prepared by copolymerizing a conjugated diene containing from 4 to 10 carbon atoms with at least one



substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine, and alkyl substituted quinoline wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15 and wherein R′ is se-

lected from the group consisting of a hydrogen atom and methyl radical.

6. A propellant composition according to claim **1** wherein said rubbery material is a copolymer prepared by copolymerizing a conjugated diene containing from 4 to 10 carbon atoms per molecule with acrylic acid.

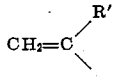
7. A propellant composition according to claim **1** wherein said burning rate depressing agent is ammonium fluoborate.

8. A propellant composition according to claim **1** wherein said burning rate depressing agent is hydrazine dihydrochloride.

9. A propellant composition according to claim **1** wherein said burning rate depressing agent is barium periodate.

10. A propellant composition according to claim **1** wherein said burning rate depressing agent is ferric oxalate.

11. A propellant composition according to claim **1** wherein said oxidant component is ammonium perchlorate, said rubbery material is a copolymer prepared by copolymerizing a conjugated diene containing from 4 to 10 carbon atoms with at least one



substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine, and alkyl substituted quinoline wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15 and wherein R′ is selected from the group consisting of a hydrogen atom and a methyl radical, and said burning rate depressing agent is hydrazine dihydrochloride.

12. A propellant composition according to claim **11** wherein said rubbery material is a copolymer of 1,3-butadiene with 2-methyl-5-vinylpyridine.

13. A propellant composition according to claim **12** wherein said burning rate depressing agent is ammonium fluoborate.

14. A propellant composition according to claim **12** wherein said burning rate depressing agent is hydrazine hydrochloride.

15. A propellant composition according to claim **12** wherein said burning rate depressing agent is barium periodate.

16. A propellant composition according to claim **12** wherein said burning rate depressing agent is ferric oxalate.

17. A propellant composition according to claim **6** wherein said burning rate depressing agent is ammonium fluoborate.

18. A propellant composition according to claim **6** wherein said burning rate depressing agent is barium periodate.

19. A propellant composition according to claim **1** wherein the amount of burning rate depressing agent is within the range of 2 to 6 weight percent of the total composition.

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