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3,027,282

COMPOSITE PROPELLANTS CONTAINING MODIFYING AGENTS

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No Drawing. Filed Dec. 29, 1958, Ser. No. 783,615
18 Claims. (Cl. 149-19)

This invention relates to solid propellant compositions. In one aspect, this invention relates to solid propellant compositions having a reduced temperature sensitivity with respect to burning rate.

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. They 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 nitrate 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 Serial No. 284,447, filed April 25, 1952, by W. B. Reynolds and J. E. Pritchard.

One disadvantage of solid propellant compositions is that the burning rate thereof is dependent upon the temperature of the propellant itself. In view of the wide fluctuations in the prevailing temperatures at which said propellants are utilized, propellants having a low temperature sensitivity with respect to burning rate are desired. Temperature sensitivity, π_p , as employed herein, can be defined as the percent change in the burning rate per degree Fahrenheit change in temperature, at a constant pressure, commonly 600 or 100 p.s.i.g.

I have discovered that the burning rate of solid propellant compositions formulated with an oxidizer component comprised principally of ammonium nitrate or an alkali metal nitrate can be advantageously modified by including therein a heteropolymolybdate and/or vanadium pentoxide. Either of said modifying agents can be used to modify the burning rate and effect a decrease in the temperature sensitivity of said burning rate. However, when said modifying agents are used in combination a synergistic effect is obtained, i.e., the obtained decrease in temperature sensitivity of the burning rate is greater than would be expected from the use of either of said modifying agents alone in like amount.

Thus, broadly speaking, the present invention resides

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in a solid propellant composition comprising an oxidizer component, a binder component, and a modifying agent adapted to decrease the burning rate temperature sensitivity of said propellant, as discussed further hereinafter.

5 An object of this invention is to provide an improved solid propellant composition. Another object of this invention is to provide an additive or modifying agent for decreasing the burning rate temperature sensitivity of solid propellant compositions. Another object of this invention is to provide an improved solid propellant composition having a decreased burning rate temperature sensitivity. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

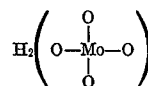
15 Thus, according to the invention there is provided a solid propellant composition comprised of: a base propellant comprising an oxidizer component selected from the group of solid inorganic oxidizing salts consisting of ammonium nitrate, the alkali metal nitrates, ammonium perchlorate, the alkali metal perchlorates, and mixtures thereof, at least 75 weight percent of said oxidizer component being at least one of said nitrates, and a binder component comprised of a rubbery material selected from the group consisting of natural rubber, synthetic rubbery polymers, and mixtures thereof; and a modifying agent selected from the group consisting of (1) vanadium pentoxide, (2) a heteropolymolybdate characterized by the formula



30 wherein: X is selected from the group consisting of ammonium and the alkali metals sodium, potassium, lithium, rubidium, and caesium; n is the valence of the anion group ($Z_aMo_bO_c$) and is a positive whole integer of from 2 to 8; Z is selected from the group consisting of phosphorus and silicon; a is a positive whole integer of from 1 to 2; b is a positive whole integer of from 6 to 18; and c is a positive whole integer of from 24 to 62, (3) mixtures of said heteropolymolybdates, and (4) mixtures of said (1) and said (2); said modifying agents (1), (2), and (3) being present in amounts ranging from 0.1 to 6 parts by weight per 100 parts by weight of said base propellant; and said modifying agent (4) being present in amounts ranging from 0.1 to 12 parts by weight per 100 parts by weight of said base propellant.

45 The results obtained when using the modifying agents of the invention are believed to be unique for said modifying agents and said nitrate containing propellants. Other compounds of an analogous type do not give a reduction in the burning rate temperature sensitivity. For example, metal oxides such as nickel oxide, titanium dioxide, cobalt oxide, etc., caused and increase in the burning rate temperature sensitivity rather than a decrease. Furthermore, as disclosed and claimed in my copending application Serial No. 783,619, filed December 29, 1958, said heteropolymolybdates decrease the burning rate of solid propellant compositions wherein the major portion of the oxidizer component is a perchlorate such as ammonium perchlorate or the alkali metal perchlorates, whereas in the instant invention the burning rate of said nitrate containing propellants is increased.

60 The term "heteropolymolybdate," as used herein, can be defined as a complex of molybdic acid with either phosphoric acid or silicic acid. Molybdic acid can be presented by the formula



70 and as hydrated complexes of the oxide MoO_3 . The heteropolymolybdates used in the practice of the invention are the ammonium and the alkali metal salts of com-

plex anions resulting from the condensation of molybdic acid with either phosphoric acid or silicic acid. The mechanism of said condensation reaction is not fully understood. Many of the salts thus formed have definite crystal structures while others are amorphous. The compounds used in the practice of the invention can be classified by the ratio of hetero atoms (phosphorus or silicon in the practice of the invention) to molybdenum atoms.

Specific examples of said heteropolymolybdates useful in the practice of the invention include, among others, the following:

$K_4SiMo_{12}O_{40}$
Tetrapotassium silico-12-molybdate
 $(NH_4)_3PMo_{12}O_{40}$
Triammonium phospho-12-molybdate
 $Na_3PMo_{12}O_{40}$
Trisodium phospho-12-molybdate
 $K_3PMo_{12}O_{40}$
Tripotassium phospho-12-molybdate
 $Li_4SiMo_{12}O_{40}$
Tetralithium silico-12-molybdate
 $Na_4SiMo_{12}O_{40}$
Tetrasodium silico-12-molybdate
 $Rb_4SiMo_{12}O_{40}$
Tetrarubidium silico-12-molybdate
 $Cs_4SiMo_{12}O_{40}$
Tetracesium silico-12-molybdate
 $(NH_4)_4SiMo_{12}O_{40}$
Tetraammonium silico-12-molybdate
 $Na_6P_2Mo_{18}O_{62}$
Hexasodium 2-phospho-18-molybdate
 $(NH_4)_2P_2Mo_{18}O_{62}$
Diammonium-2-phospho-18-molybdate
 $Na_8SiMo_{12}O_{42}$
Octasodium silico-12-molybdate
 $K_7PMo_{11}O_{39}$
Heptapotassium phospho-11-molybdate
 $(NH_4)_5PMo_9O_{32}$
Pentaammonium phospho-9-molybdate
 $Cs_6SiMo_9O_{32}$
Hexacesium silico-9-molybdate
 $(NH_4)_7PMo_6O_{24}$
Heptaammonium phospho-6-molybdate
 $(NH_4)_6P_2Mo_{18}O_{62}$
Hexaammonium 2-phospho-18-molybdate

The formulas as given above are for the anhydrous salts. Hydrated salts of said compounds are also applicable in the practice of the invention. An example of such a hydrate is $(NH_4)_6P_2Mo_{18}O_{62} \cdot 11H_2O$, also written as $3(NH_4)_2O \cdot P_2O_5 \cdot 18MoO_3 \cdot 11H_2O$. For many of the hydrates the water of crystallization amounts to less than 30 mols of water per mol of heteropolymolybdate molecule. If desired, the water of hydration can be decreased before or during preparation of the propellant, for example, by the application of heat during the mixing or milling operation, and/or by carrying out said mixing or milling operation at reduced pressures.

A review on the structure, properties and the preparation of heteropolymolybdates is given by Killeffer and Linz, "Molybdenum Compounds," chapter 8, pages 87-94, Interscience Publishers, New York (1952).

The quantity of said additive or modifying agent employed in the practice of the invention is usually in the range of 0.1 to 6 parts by weight per 100 parts by weight of base propellant when the modifying agent is vanadium pentoxide, one of said heteropolymolybdates, or a mixture of said heteropolymolybdates. However, in some instances greater amounts can be used with advantageous results. When the additive or modifying agent is a mixture of vanadium pentoxide and one of the above-described heteropolymolybdates, the amount employed is usually in the range of 0.1 to 12 parts by weight per 100 parts by weight of said base propellant. How-

ever, in some instances greater amounts can be used with advantageous results. It is preferred that the ratio of said vanadium pentoxide to said heteropolymolybdate in said mixture be in the range of 0.5 to 4.0, in parts by weight, more preferably about 2; and that the amount of vanadium pentoxide and the amount of heteropolymolybdate in said mixture each not exceed 6 parts by weight per 100 parts of base propellant.

As used herein and in the claims, unless otherwise specified, the term "base propellant" is defined as the binder component plus the oxidant component. The rubbery material employed in the binder component of the propellant compositions of the invention can be a natural rubber, a synthetic rubbery polymer, or a mixture of natural rubber and said rubbery polymer. The term "rubbery polymer" as used herein and in the claims, unless otherwise specified is defined as including all rubbery polymers of olefins and diolefins which are prepared by either mass or emulsion polymerization. Some examples of suitable rubbery polymers are polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes with comonomers such as styrene, and copolymers of conjugated dienes with polymerizable heterocyclic nitrogen bases. Said copolymers of conjugated dienes with polymerizable heterocyclic bases comprise a preferred class of rubbery polymers for use in the binder component of the propellants of the invention. A presently preferred rubbery polymer is a copolymer of 1,3-butadiene with 2-methyl-5-vinylpyridine.

Said preferred class of rubbery polymers prepared by copolymerizing a conjugated diene with a heterocyclic nitrogen base can vary in consistency from 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) up to 100. The rubbery copolymers most frequently preferred have Mooney values in the range between 5 and 50. They may be prepared by any polymerization methods known to the art, e.g., mass or emulsion polymerization. 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 vinylpyridine 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 and 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 are those of the pyridine, quinoline, and isoquinoline series which are copolymerizable with a conjugated diene and contain one, and only one,

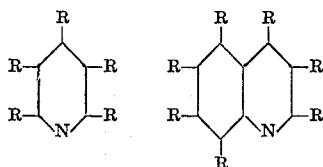


substituent wherein R' is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl (isopropenyl) group. Of these, the compounds of the pyridine series are of the greatest interest commercially at present. Various substituted derivatives are also applicable but the total number of

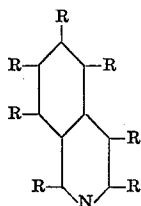
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carbon atoms in the groups attached to the carbon atoms of the heterocyclic nucleus should not be greater than 15 because the polymerization rate decreases somewhat with increasing size of the alkyl group. Compounds where the alkyl substituents are methyl and/or ethyl are available commercially.

These heterocyclic nitrogen bases have the formula



or



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-vinylpyridine;
 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;
 3-vinyl-6,7-di-n-propylquinoline;
 2-methyl-4-nonyl-6-vinylpyridine;
 4-(alpha-methylvinyl)-8-dodecylquinoline;
 3-vinylisoquinoline;
 1,6-dimethyl-3-vinylisoquinoline;
 2-vinyl-4-benzylquinoline;
 3-vinyl-5-chloroethylquinoline-3-vinyl-5,6-dichloro-isoquinoline;
 2-vinyl-6-ethoxy-7-methylquinoline;
 3-vinyl-6-hydroxymethylisoquinoline;

and the like.

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

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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 United States Patents 2,583,277; 2,595,892; 2,609,362; 2,614,100; 2,647,109; and 2,665,269.

The binder contains rubbery polymers of the type heretofore described and, in addition, there can be present one or more reinforcing agents, plasticizers, 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 5 to 75 percent by weight.

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
40 Plasticizer	0-100
Wetting agent	0-10
Antioxidant	0-3
Vulcanization accelerator	0-5
Sulfur	0-2
45 Metal oxide	0-5

Reinforcing agents which can be employed include carbon black, wood flour, lignin, and various reinforcing resins such as styrene-divinylbenzene, methyl acrylate-divinylbenzene, 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), 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-trioxundecyl) methane, 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-butyl-phenol), 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 supplied by the R. F. Vanderbilt Company and 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 nitrate, the alkali metal nitrates, ammonium perchlorate, and the alkali metal perchlorates. As used herein, the term "alkali metal" includes sodium, potassium, lithium, cesium, and rubidium. Ammonium nitrate is the presently preferred oxidizer. Mixtures of said oxidizers are also applicable. When mixtures of said oxidizers are used, one of said nitrates, preferably ammonium nitrate, should be at least 75 weight percent of the mixture. In the preparation of the solid rocket propellant compositions of the invention, said oxidizers are ground to a particle size preferably within the range between 20 and 200 microns average particle size. The most preferred particle size is from about 40 to about 60 microns. The amount of oxidizer used is a major amount of the total composition and is usually within the range of about 75 to about 95 weight percent of the base propellant, i.e., binder plus oxidizer. It is frequently preferred to use a phase stabilized ammonium nitrate. One method of phase stabilizing ammonium nitrate comprises mixing about 10 parts by weight of a potassium salt (usually potassium nitrate) with about 90 parts by weight of ammonium nitrate along with some water, heating the mixture to about 140° F., drying, and then grinding the resulting mixture to the desired particle size.

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 blade mixer can be employed. In the final propellant the binder component forms a continuous phase with the oxidizer component being a discontinuous phase. One procedure for blending the propellant ingredients utilizes a stepwise addition of oxidizer ingredient. The binder ingredients are first mixed to form a binder mixture and the oxidizer ingredient, having the modifying agent or additive of the invention dry blended therewith, is then added to said binder mixture in increments, usually 3 to 5, but more 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 extrusion, or compression molding, according to procedures known to those skilled in the art.

After forming, the rocket grains are generally cured. The curing temperature will generally be in the range between about 70 to 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. The curing time will generally range from around 2 hours, when the higher curing temperatures are employed, to 7 days when curing is effected at the lower temperatures.

The following example will serve to further illustrate the invention:

EXAMPLE

A rubbery copolymer was prepared by emulsion poly-

merization of 1,3-butadiene and 2-methyl-5-vinylpyridine at 41° F. The polymerization recipe was as follows:

Recipe

	Parts by weight
1,3-butadiene -----	90
2-methyl-5-vinylpyridine -----	10
Water -----	200
Potassium soap -----	6
Potassium chloride -----	0.1
Sodium salt of condensed alkylaryl sulfonic acid -----	0.3
Tetrasodium salt of ethylenediamine-tetraacetic acid -----	0.005
Tertiary dodecyl mercaptan (modifier) -----	0.6-0.8
Ferrous sulfate heptahydrate -----	0.2
Potassium pyrophosphate -----	0.253
Para-menthane hydroperoxide -----	0.135

A total of 55 runs were made using the above recipe. The average conversion for these runs was 85 percent in 17.0 hours. The polymerization was shortstopped with 0.15 part by weight per 100 parts by weight of rubber of potassium dimethyl dithiocarbamate, and 1.75 parts by weight per 100 parts by weight of rubber of phenyl-beta-naphthylamine was added as a stabilizer. The latex was masterbatched with 19.5 parts by weight of a low abrasion furnace carbon black per 100 parts by weight of rubber. The black masterbatch was then coagulated with acid, the crumb was washed with water, and then dried.

The carbon black content of the above-described copolymer product was increased to 22 parts by weight per 100 parts by weight of rubber by milling an additional 2.5 parts of said carbon black into said copolymer. Three parts by weight per 100 parts by weight of rubber of Flexamine, a physical mixture containing 65% of a complex diarylamine-ketone reaction product and 35% of N,N'-diphenyl-p-phenylene-diamine, was also milled into said copolymer.

The thus prepared rubber masterbatch was used to prepare a binder having the following composition:

	Parts by weight
90/10 copolymer -----	100
Carbon black -----	22
Phenyl-beta-naphthylamine -----	1.75
Flexamine -----	3
ZP-211 ¹ -----	20
Magnesium oxide -----	5

¹ Crude di(1,4,7-trioxadecyl) methane, [C₄H₉OOC₂H₄O]CH₂ which has been stripped of light material.

This binder in amounts of 16.5 parts by weight was blended on a roll mill with 83.5 parts by weight of ammonium nitrate to form a base propellant. The ammonium nitrate has been ground to pass a 140 mesh screen and had a weight average particle size of 40 microns.

Modifying agents in accordance with the invention were then added to different portions of said base propellant. Table I given below shows the amounts used per 100 parts of base propellant. The resulting mixtures were blended and then extruded into cylindrical strands having a diameter of 3/16 inch. The strands were cured for 24 hours at a temperature of about 200° F. The cured strands were cut into 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 pressured to the desired pressure (600 or 1000 p.s.i.g.) with nitrogen. The strands were ignited, and the time required for the propellant to burn between two fusible wires spaced five inches apart was recorded. By determining the strand burning rate at different temperatures in the range from about -70° F. to +170° F., and at a given constant

pressure, the temperature sensitivity of the burning rate can be computed from the equation

$$\pi_p = \frac{\left(\ln \frac{r_1}{r_2}\right) 100}{T_1 - T_2}$$

wherein r_1 and r_2 are the burning rates at temperatures T_1 and T_2 respectively. Said temperatures are expressed in degrees Fahrenheit and T_1 is greater than T_2 . Thus the units for π_p are in percent per degree Fahrenheit.

The results of said burning rate tests are given below in Table I:

TABLE I.—EFFECT OF MODIFYING AGENTS ON BURNING RATE AND BURNING RATE TEMPERATURE SENSITIVITY

Propellant No.	Modifying Agent ¹		Burning Rate @ 70° F., in./sec.		Burning Rate Temperature Sensitivity, π_p , at 1,000 p.s.i.g.		
	Type	Parts by Weight	600 p.s.i.g.	1,000 p.s.i.g.	-70 to 70° F.	70 to 170° F.	-70 to 170° F.
1-----	None-----	0	0.059	0.089	0.165	0.176	0.171
2-----	SiMo ₁₂ -----	2	0.103	0.129	-----	0.14	-----
3-----	SiMo ₁₂ -----	4	0.108	0.146	-----	0.126	-----
4-----	SiMo ₁₂ -----	6	0.115	0.146	-----	0.08	-----
5-----	P ₂ Mo ₁₈ -----	2	0.093	0.122	-----	0.11	-----
6-----	P ₂ Mo ₁₈ -----	4	0.093	0.125	-----	0.12	-----
7-----	P ₂ Mo ₁₈ -----	6	0.088	0.111	-----	0.13	-----
8-----	P ₂ Mo ₁₈ -----	8	0.113	0.143	-----	0.11	-----
9-----	V ₂ O ₅ -----	2	0.119	0.162	0.12	0.13	0.126
10-----	V ₂ O ₅ -----	4	0.135	0.171	0.12	0.05	0.089
11-----	V ₂ O ₅ -----	6	0.081	0.128	0.08	0.13	0.098
12-----	V ₂ O ₅ -----	4	0.093	-----	0.00	0.09	0.043
13-----	SiMo ₁₂ -----	2	-----	-----	-----	-----	-----
14-----	V ₂ O ₅ -----	4	0.102	-----	0.08	0.05	0.065
	SiMo ₁₂ -----	2	-----	-----	-----	-----	-----
	V ₂ O ₅ -----	4	0.146	-----	0.09	0.07	0.08
	SiMo ₁₂ -----	6	-----	-----	-----	-----	-----

¹ SiMo₁₂ is Na₄SiMo₁₂O₄₀ and P₂Mo₁₈ is Na₆P₂Mo₁₈O₆₂. The parts by weight is in terms of parts by weight per 100 parts by weight of base propellant. The moisture content (based on loss in weight on drying at 89.5° C. at a pressure of less than 2 mm. Hg for 39 hours) of the Na₄SiMo₁₂O₄₀ was 6.2 weight percent, and for the Na₆P₂Mo₁₈O₆₂ was 9.1 weight percent. At least some of said moisture content was water of hydration. The above tests were run using undried materials.

² The lower temperature in these runs was -75° F. instead of -70° F.

A comparison of the data for propellants 2, 3 and 4 with the data for propellant 1, the control propellant, shows that tetrasodium silico-12-molybdate



increases the burning rate of the propellant and decreases the temperature sensitivity of said burning rate.

A comparison of the data for propellants 5-8, inclusive, with the data for propellant 1, the control propellant, shows that hexasodium 2-phospho-18-molybdate increased the burning rate of the propellant and also effected a substantial decrease in the temperature sensitivity of said burning rate.

A comparison of the data for propellants 9-11, inclusive, with the data for propellant 1, the control propellant, shows that vanadium pentoxide increased the burning rate of said propellant and also effected a substantial decrease in the temperature sensitivity of said burning rate.

Particular attention is invited to the data obtained with propellants 12, 13, and 14 in which a combination propellant modifying agent or additive consisting of a mixture of vanadium pentoxide and tetrasodium silico-12-molybdate was used. A comparison of the data for said propellants 12, 13, and 14 with the data for propellant 1, the control propellant, shows that this combination modifying agent also increased the burning rate of the propellant and effected a very substantial decrease in the temperature sensitivity of said burning rate. It will be noted that the total amount of modifying agent used in propellants 12 and 13 was 6 parts by weight. Thus, a comparison should be made between propellants 13, 11, and 4. This comparison will show 6 parts of the combination modifying agent used in propellant 13 decreased the temperature sensitivity over the range from 70 to

170° F. more than a like amount of the single modifying agent used in either of propellants 11 or 4.

A comparison of the data for propellants 12-14 wherein the combination modifying agent was used, with the data for propellants 2-4 and propellants 9-11, shows that the temperature sensitivity was in all runs essentially as low as, or lower, than was obtained when using like amounts of one of the single modifying agents.

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 75 to 95 percent of an oxidizer component selected from the group of solid inorganic oxidizing salts consisting of ammonium nitrate, the alkali metal nitrates, ammonium perchlorate, the alkali metal perchlorates, and mixtures thereof, at least 75 weight percent of said oxidizer component being at least one of said nitrates, and from 25 to 5 weight percent of a binder component comprised of a rubbery material selected from the group consisting of natural rubber, synthetic rubbery polymers, and mixtures thereof; and a modifying agent selected from the group consisting of (1) vanadium pentoxide, (2) a heteropolymolybdate characterized by the formula



wherein: X is selected from the group consisting of ammonium and the alkali metals sodium, potassium, lithium, rubidium, and cesium; n is the valence of the anion group ($\text{Z}_a\text{Mo}_b\text{O}_c$) and is a positive whole integer of from 2 to 8; Z is selected from the group consisting of phosphorus and silicon; a is a positive whole integer of from 1 to 2; b is a positive whole integer of from 6 to 18; and c is a positive whole integer of from 24 to 62, (3) mixtures of said heteropolymolybdates, and (4) mixtures of said (1) and said (2); said modifying agents (1), (2), and (3) being present in amounts ranging from 0.1 to 6 parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder components; and said modifying agent (4) being present in amounts ranging from 0.1 to 12 parts by

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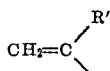
weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component.

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

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

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

6. A propellant composition according to claim 1 wherein said modifying agent is vanadium pentoxide.

7. A propellant composition according to claim 1 wherein said modifying agent is hexaammonium 2-phospho-18-molybdate.

8. A propellant composition according to claim 1 wherein said modifying agent is hexasodium 2-phospho-18-molybdate.

9. A propellant composition according to claim 1 wherein said modifying agent is hexapotassium 2-phospho-18-molybdate.

10. A propellant composition according to claim 1 wherein said modifying agent is tetra-rubidium silico-12-molybdate.

11. A propellant composition according to claim 1 wherein said modifying agent is tetra-cesium silico-12-molybdate.

12. A propellant composition according to claim 1 wherein said modifying agent is tetra-sodium silico-12-molybdate.

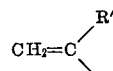
13. A propellant composition according to claim 1 wherein said modifying agent is a mixture of vanadium pentoxide and one of said heteropolymolybdates.

14. A propellant composition according to claim 1 wherein said modifying agent is a mixture of vanadium pentoxide and tetra-sodium silico-12-molybdate.

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15. A propellant composition according to claim 1 wherein said modifying agent is a mixture of, in parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component, 4 parts of vanadium pentoxide and 2 parts of tetra-sodium silico-12-molybdate.

16. A propellant composition according to claim 1 wherein said oxidizer component is a phase stabilized ammonium nitrate, 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 modifying agent is a mixture of, in parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component, 4 parts of vanadium pentoxide and 2 parts of tetra-sodium silico-12-molybdate.

17. A propellant composition according to claim 16 wherein said rubbery material is a copolymer of 1,3-butadiene with 2-methyl-5-vinylpyridine.

18. A propellant composition according to claim 1 wherein said modifying agent is a mixture of, in parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component, 4 parts of vanadium pentoxide and 6 parts of tetra-sodium silico-12-molybdate.

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