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COMPOSITE PROPELLANTS CONTAINING A BURNING RATE DEPRESSANT

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16 Claims. (Cl. 149—19)

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. 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 heterocycle nitrogen base compound, which after incorporation is cured by a quarternization 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.

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.

I have discovered that the burning rate 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 a group of heteropolymolybdates defined hereinafter. 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 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 heteropolymolybdate as a burning rate depressing agent. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

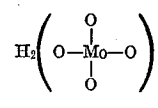
Thus, according to the invention there is provided a solid propellant composition, suitable for use in a rocket motor for developing thrust, comprised of: a base propellant comprising an oxidizer component selected from the group of solid inorganic oxidizing salts consisting of ammonium perchlorate, the alkali metal perchlorates, ammonium nitrate, the alkali metal nitrates, and mixtures thereof, at least 75 weight percent of said oxidizer component being at least one of said perchlorates, and a binder component comprised of a rubbery material selected from the group consisting of natural rubber and synthetic rubbery polymers and mixtures thereof; and from 0.1 to 15 parts by weight per 100 parts by weight of said base propellant of a heteropolymolybdate burning rate depressing agent selected from the group consisting of heteropolymolybdates characterized by the formula

$$X_nZ_aMo_bO_c$$

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 ($Z_aMo_bO_c$) 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.

The results obtained using the above-identified heteropolymolybdates are believed unique for said perchlorate containing propellants because as disclosed and claimed in my copending application, Serial No. 783,615, filed December 29, 1958, said heteropolymolybdates increase the burning rate of solid propellant compositions wherein the major portion of the oxidizer component is a nitrate such as ammonium nitrate or the alkali metal nitrates, whereas in the instant invention the burning rate of said perchlorate containing propellants is decreased.

As used herein, the term "heteropolymolybdate" refers to a complex of molybdic acid with either phosphoric acid or silicic acid. Molybdic acid can be represented by the formula



and as hydrated complexes of the oxide MoO_3. Said heteropolymolybdates used in the practice of the invention are complex ions 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) to molybdenum atoms.

Specific examples of said heteropolymolybdates which are 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
$(NH_4)_2P_2Mo_{12}O_{42}$
Diammonium 2-phospho-12-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 phosphate-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 these compounds are also applicable for use 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. 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 amount of said heteropolymolybdates utilized as burning rate depressants in the practice of the invention is within the range of 0.1 to 15 parts by weight, preferably 0.2 to 5 parts by weight, per 100 parts by weight 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.

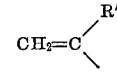
Said preferred class of rubbery polymers prepared by copolymerizing a conjugated diene with a heterocyclic

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.

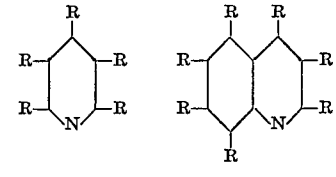
Instead of using a single conjugated diene, a mixture of conjugated dienes can be employed. Thus, a mixture of 1,3-butadiene and isoprene can be employed as the conjugated diene portion of the monomer system.

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,

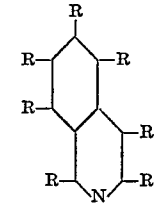


substituent wherein R′ is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl (isopropenyl) group. Of these, the compounds of the pyridine series are of the greatest interest commercially at present. Various substituted derivatives are also applicable but the total number of 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-methylphenyl)-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-dichloroisoquinoline; 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 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 hereinbefore 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
Plasticizer	0–100
Wetting agent	0–10
Antioxidant	0–3
Vulcanization accelerator	0–5
Sulfur	0–2
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-2HX (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, 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-tertbutylphenol), 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 single 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 preferably ammonium perchlorate, should be 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 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.

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 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 extrusion, or compression molding, utilizing techniques known to those skilled in the art.

The formulated grains are usually cured before use. The curing temperature would 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

A rubbery copolymer was prepared by emulsion polymerization 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	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 short-stopped 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 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 blend 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 percent of a complex diarylamine-ketone reaction product and 35 percent of N,N'-diphenyl-p-phenylenediamine, was also milled into said copolymer.

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

	Parts by weight
90/10 copolymer	100
Carbon black	22
Butarez 25 [1]	20
Butyl-Eight [2]	2
Sulfur	1.75
Zinc oxide	3
Magnesium oxide	5
Flexamine [3]	3
Phenyl-beta-naphthylamine	1.75

[1] Liquid polybutadiene plasticizer.
[2] Activated dithiocarbamate.
[3] 65 percent diarylamine-ketone reaction product and 35 percent N,N'-diphenyl-p-phenylenediamine.

This binder was used to prepare base propellant compositions containing 15 parts by weight of said binder for each 85 parts by weight of ammonium perchlorate. The perchlorate was a mixture of two batches of the ground salt. Thirty parts by weight of one batch having a weight average size of 40 microns was mixed with 70 parts by weight of another batch having a weight average size of 200 microns. Both batches were substantially free of particles larger than 140 mesh (105 micron screen opening).

The base propellants were prepared by first mixing equal parts by weight of the binder and the oxidizer. This uniform blend or materbatch was divided into portions. Each portion was then admixed with additional oxidizer, so as to provide a base propellant containing 85 parts of oxidizer for each 15 parts of binder. The desired candidate burning rate depressants in amounts of 2 parts by weight per 100 parts by weight of base propellant was then blended into said base propellants. The propellant compositions were then extruded to form cylindrical strands having a diameter of 9/16 inch. The strands were cured for 24 hours at a temperature of about 200° F. 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 (300, 600 or 1000 p.s.i.). 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 was computed from the results obtained. The resulting data are presented in Table I below. At a pressure of 300 p.s.i. the tetrasodium silico-12-molybdate effected a 36 percent depression of the burning rate. At pressures of 600 and 1000 p.s.i., the tetrasodium silico-12-molybdate effected a 44 and a 45 percent depression in burning rate, respectively. At a pressure of 300 p.s.i. the trisodium phospho-12-molybdate effected a 4 percent depression of the burning rate. At pressures of 600 and 1000 p.s.i., the trisodium phospho-12-molybdate effected 11 and 9 percent depressions in burning rate, respectively.

TABLE I.—DEPRESSION OF BURNING RATE OF AMMONIUM PERCHLORATE PROPELLANTS

Run No.	Additive		Burning Rate, In./Sec.			Percent Depression		
	Type [1]	Amount, Parts by Wt. [2]	300 p.s.i.	600 p.s.i.	1,000 p.s.i.	300 p.s.i.	600 p.s.i.	1,000 p.s.i.
1	None	0	0.690	1.090	1.410	0	0	0
2	Tetrasodium-silico-12-molybdate	2	0.440	0.610	0.782	36	44	45
3	Trisodium phospho-12-molybdate	2	.066	0.975	1.29	4	11	9

[1] 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 tetrasodium silico-12-molybdate was 6.2 weight percent, and for the trisodium phospho-12-molybdate was 7.1 weight percent. At least some of said moisture content was water of hydration. The above tests were run using undried materials.
[2] Parts by weight per 100 parts of base propellant.

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, comprised of: from 75 to 95 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 75 weight percent of said oxidizer component being at least one of said perchlorates, and from 25 to 5 weight percent of a binder component comprised of a rubbery material selected from the group consisting of natural rubber and synthetic rubbery polymers and mixtures thereof; and from 0.1 to 15 parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component of a heteropolymolybdate burning rate depressing agent selected from the group consisting of heteropolymolybdates characterized by the formula

$$X_nZ_aMo_bO_c$$

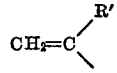
wherein: X is selected from the group consisting of ammonium and the alkali metals sodium, potassium, lithium, rubidium, and cesium, *n* is the valence of the anion group ($Z_aMo_bO_c$) and is a positive whole integer of from 2 to 8; Z is selected from the group consisting of phosphorus and silicon; *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.

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

6. A propellant composition according to claim 1 wherein said burning rate depressing agent is triammonium phospho-12-molybdate.

7. A propellant composition according to claim 1 wherein said burning rate depressing agent is trisodium phospho-12-molybdate.

8. A propellant composition according to claim 1 wherein said burning rate depressing agent is tripotassium phospho-12-molybdate.

9. A propellant composition according to claim 1 wherein said burning rate depressing agent is tetrarubidium silico-12-molybdate.

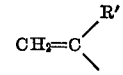
10. A propellant composition according to claim 1 wherein said burning rate depressing agent is tetracesium silico-12-molybdate.

11. A propellant composition according to claim 1 wherein said burning rate depressing agent is hexasodium 2-phospho-18-molybdate.

12. A propellant composition according to claim 1 wherein said burning rate depressing agent is tetrasodium silico-12-molybdate.

13. A propellant composition according to claim 1 wherein the amount of said burning rate depressing agent is within the range of 0.2 to 5 parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component.

14. 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 tetrasodium silico-12-molybdate.

15. A propellant composition according to claim 14 wherein said rubbery material is a coplymer of 1,3-butadiene with 2-methyl-5-vinylpyridine.

16. A propellant composition according to claim 14 wherein said burning rate depressing agent is tetrasodium silico-12-molybdate.

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