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3,026,672

COMPOSITE PROPELLANT CONTAINING BURNING RATE DEPRESSANT AND METHOD OF USE
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20 Claims. (Cl. 60—35.4)

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 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.

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 the 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 the group consisting of hydroxylamine, inorganic salts of hydroxylamine, semicarbazide, and inorganic salts of semicarbazide. Thus, broadly speaking, the present invention resides in a solid

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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 burning rate depressing agent selected from the group consisting of hydroxylamine, inorganic salts of hydroxylamine, semicarbazide, and inorganic salts of semicarbazide. 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 a major portion 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 20 parts by weight per 100 parts by weight of said base propellant of a burning rate depressing agent selected from the group consisting of hydroxylamine, inorganic salts of hydroxylamine, semicarbazide, inorganic salts of semicarbazide, and mixtures thereof.

As used herein and in the claims, unless otherwise specified, the term "inorganic salts" refers to salts of hydroxylamine or salts of semicarbazide which are formed by reacting said compounds with the various mineral acids. Various procedures for the preparation of said salts are known to those skilled in the art. The preferred inorganic salts are those of the strong mineral acids, e.g., hydrochloric acid, nitric acid, perchloric acid, and sulfuric acid. Examples of said inorganic salts include, among others, the following:

45	$\text{NH}_2\text{OH} \cdot \text{HClO}_4$ -----	Hydroxylamine perchlorate
	$\text{NH}_2\text{OH} \cdot \text{HCl}$ -----	Hydroxylamine hydrochloride.
	$2\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$ -----	Hydroxylamine sulfate.
50	$\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$ -----	Hydroxylamine acid sulfate.
	$\text{NH}_2\text{OH} \cdot \text{HNO}_3$ -----	Hydroxylamine nitrate.
	$3\text{NH}_2\text{OH} \cdot \text{H}_3\text{BO}_3$ -----	Hydroxylamine borate.
	$3\text{NH}_2\text{OH} \cdot \text{H}_3\text{PO}_4$ -----	Hydroxylamine phosphate.
55	$2\text{NH}_2\text{OH} \cdot \text{H}_2\text{SiF}_6$ -----	Hydroxylamine fluorosilicate.
	$\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{HClO}_4$	Semicarbazide perchlorate.
	$\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{HCl}$	Semicarbazide hydrochloride.
60	$2\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{H}_2\text{SO}_4$	Semicarbazide sulfate.
	$\text{H}_2\text{N}-\text{CO}-\text{NHNH}_2 \cdot \text{HNO}_3$	Semicarbazide nitrate.

The amount of said burning rate depressants utilized in the practice of the invention is usually within the range of 0.1 to 20 parts by weight, preferably 0.5 to 10 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

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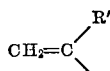
rubbery material employed in the binder component of the propellant compositions of the invention can be a natural rubber, a synthetic rubbery polymer, or a mixture of natural rubber and said rubbery polymer. The term "rubbery polymer" as used herein and in the claims, unless otherwise specified is defined as including all rubbery polymers of olefins and diolefins which are prepared by either mass or emulsion polymerization. Rubbery polymers having a Mooney value (ML-4 at 212° F.) in the range of 10 to 60 are generally preferred. 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 10 and 60. 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.

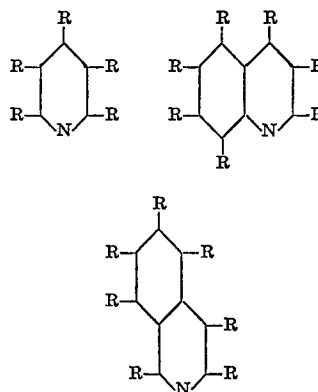
The polymerizable heterocyclic nitrogen bases which are applicable for the production of the polymeric materials are those of the pyridine, quinoline, and isoquinoline series which are copolymerizable with a conjugated diene and contain one, and only one,



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.

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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-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

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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 25 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-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, 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.

One presently preferred plasticizer is a liquid polybutadiene prepared by mass polymerization in the presence of finely divided sodium as the catalyst according to the method of Crouch 2,631,175. Broadly, such plasticizers which can be used in accordance with this invention comprise liquid polymers prepared from conjugated diolefin hydrocarbons such as 1,3-butadiene and isoprene, the liquid polymers having a viscosity of 100 to 5000 Saybolt Furol Seconds at 100° F. Polymers having a viscosity from about 100 to about 2500 Saybolt Furol Seconds are presently preferred. These liquid polymers can be prepared by emulsion polymerization using large amounts of modifiers in accordance with the teaching of Frolich et al. 2,500,983 although they are preferably prepared by the method set forth in Crouch 2,631,175. The latter method comprises mass polymerization in the presence of finely divided alkali metal and/or alkali metal hydride such as sodium, potassium, lithium, sodium hydride, potassium hydride and lithium hydride. Polymers thus prepared contain no modifiers or viscosity controlling agent and they are also free of materials which would act as inhibitors such as antioxidants and shortstops. Finely divided catalyst is used, preferably having a particle size below 200 microns, and generally below 100 microns in the range of 40 to 80 microns. The amount of catalyst employed usually does not exceed 2 parts by weight of the total monomer charged, preferably in the range of 0.5 to 1.5 parts by weight per 100 parts monomer. A more complete description of the process is set forth in the Crouch patent identified above.

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

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(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-butyl-sulphenyl 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 perchlorate, the alkali metal perchlorates, ammonium nitrate, and the alkali metal nitrates. As used herein, the term "alkali metal" includes sodium, potassium, lithium, caesium, 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 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 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

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:

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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 as shown below in Table I.

The base propellants were prepared by first mixing equal parts by weight of the binder and the oxidizer. This uniform blend or masterbatch 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 depressant in the amounts shown in the following Table I was then blended into said base propellants. The propellant compositions were then extruded to form cylindrical strands having a diameter of $\frac{3}{16}$ inch. The strands were cured for 24 hours at a temperature of about 180° 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

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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 was computed from the results obtained. The resulting data are presented in Table I below. At pressures of 300 and 1000 p.s.i. the hydroxylamine hydrochloride effected a 46 and a 47 percent depression in burning rate, respectively. At a pressure of 300 p.s.i. the semicarbazide hydrochloride effected a 31 percent depression in burning rate.

TABLE I

Depression of Burning Rate of Ammonium Perchlorate Propellants

Run No. ¹	Additive		Burning Rate, in./sec.		Depression, percent	
	Name	Amount ²	300 p.s.i.	1,000 p.s.i.	300 p.s.i.	1,000 p.s.i.
1		0	0.90	1.38		
2	Hydroxylamine hydrochloride	2	0.49	0.73	46	47
3		0	0.65			
4	Semicarbazide hydrochloride	5	0.45		31	

¹ In Run Nos. 1 and 2 the oxidizer component of the propellant was a 70/30 mixture of two batches of ammonium perchlorate which had a weight average particle size of approximately 74 and 18 microns, respectively. In Run Nos. 3 and 4 the oxidizer component of the propellant was a 70/30 mixture of two batches of ammonium perchlorate which had a weight average particle size of approximately 200 and 40 microns, respectively.

² Parts by weight per 100 parts by weight 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:

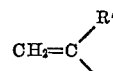
1. A solid propellant composition, comprised of: from 75 to 95 percent by weight of an oxidizer component selected from the group of solid inorganic oxidizing salts consisting of ammonium perchlorate, the alkali metal perchlorates, ammonium nitrate, the alkali metal nitrates, and mixtures thereof, at least a major portion of said oxidizer component being at least one of said perchlorates, and from 25 to 5 percent by weight 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 20 parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component of a burning rate depressing agent selected from the group consisting of hydroxyl, amine, inorganic salts of hydroxylamine, semicarbazide, inorganic salts of semicarbazide, and mixtures thereof.

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 methyl radical.

6. A propellant composition according to claim 1 wherein said burning rate depressing agent is hydroxylamine.

7. A propellant composition according to claim 1 wherein said burning rate depressing agent is hydroxylamine hydrochloride.

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

9. A propellant composition according to claim 1 wherein said burning rate depressing agent is semicarbazide hydrochloride.

10. A propellant composition according to claim 1 wherein said burning rate depressing agent is hydroxylamine sulfate.

11. A propellant composition according to claim 1 wherein said burning rate depressing agent is hydroxylamine perchlorate.

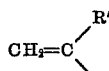
12. A propellant composition according to claim 1 wherein said burning rate depressing agent is hydroxylamine nitrate.

13. A propellant composition according to claim 1 wherein said burning rate depressing agent is semicarbazide perchlorate.

14. A propellant composition according to claim 1 wherein said burning rate depressing agent is semicarbazide nitrate.

15. A propellant composition according to claim 1 wherein the amount of burning rate depressing agent is within the range of 0.5 to 10 parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component.

16. 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 hydroxylamine hydrochloride.

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 16 wherein said burning rate depressing agent is semicarbazide hydrochloride and said rubbery material is a copolymer of 1,3-butadiene with 2-methyl-5-vinylpyridine.

19. In the method of developing thrust wherein a solid propellant charge contained in a combustion chamber of a rocket motor is ignited and then burned with the evolution of combustion gases which are exhausted from said combustion chamber, the step which comprises burning in said combustion chamber a propellant charge comprising: from 75 to 95 percent by weight 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; and from 25 to 5 percent by weight 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 20 parts by weight per 100 parts by weight of the total amount of said oxidizer component plus said binder component of a burning rate depressing agent selected from the group consisting of hydroxylamine, inorganic salts of hydroxylamine, semicarbazide, inorganic salts of semicarbazide, and mixtures thereof.

20. The method of claim 19 wherein said burning rate depressing agent is semicarbazide hydrochloride.

References Cited in the file of this patent

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,026,672

March 27, 1962

George D. Sammons

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 10, line 12, for the claim reference numeral "16" read -- 5 --.

Signed and sealed this 28th day of August 1962.

(SEAL)

Attest:

ESTON G. JOHNSON

Attesting Officer

DAVID L. LADD

Commissioner of Patents