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2,995,431

COMPOSITE AMMONIUM NITRATE PROPELLANTS CONTAINING BORON

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This invention relates to solid propellant compositions. In one aspect this invention relates to solid propellant compositions having a high burning rate. In another aspect this invention relates to solid propellant compositions containing an ammonium nitrate oxidizer and having a high burning rate.

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 a copolymer of butadiene and a vinylpyridine or other substituted heterocyclic nitrogen-base compounds, 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 Number 284,447, filed April 25, 1952, by W. B. Reynolds and J. E. Pritchard.

Ammonium nitrate containing propellants are being utilized to power take-off assists units (JATO) for aircraft. While these propellants have excellent properties and burning characteristics for this and other purposes, such as gas generators, it would be desirable to increase the burning rate and specific impulse of these ammonium nitrate propellants so as to make them more adaptable for other uses, e.g., booster propellants. It is known to use a burning rate catalyst in these propellants to increase the burning rate thereof. However, it is desirable to increase the burning rate still more than the amount which can be accomplished by the use of said burning rate catalyst.

I have now discovered that when said ammonium nitrate containing propellants contain at least 86 parts by weight of ammonium nitrate that the burning rate thereof can be increased by incorporating therein certain selected finely divided high energy additives, such as boron and or magnesium, as defined further hereinafter. It is essential that the ammonium nitrate containing propellant composition contain at least 86 parts by weight per 100 parts of total propellant of ammonium nitrate, otherwise said high energy additive will have no beneficial effect or a depressing effect upon the burning rate rather than increasing said burning rate.

An object of this invention is to provide an improved propellant composition. Another object of this invention is to provide an improved propellant composition having an increased burning rate. Still another object of this invention is to provide a solid propellant composition containing ammonium nitrate as the oxidizer component, which propellant composition has an increased burning rate, and which is suitable for use in booster propellants. Still another object of this invention is to provide a solid propellant composition containing at least 86 parts by weight per 100 parts of total propellant of ammonium nitrate and a high energy additive, such as boron and/or magnesium, as defined further hereinafter. Other aspects,

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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 comprised of, in parts by weight per 100 parts of the total composition: from 3.5 to 8 parts of a binder component comprising a rubbery polymer; from 86 to 94 parts of an ammonium nitrate oxidizer component; from 0 to 5 parts of a burning rate catalyst; and from 1 to 10 parts of a finely divided high energy additive selected from the group consisting of (a) boron, (b) magnesium, (c) mixtures of boron and magnesium, and (d) mixtures consisting of at least 50 weight percent of at least one of said (a), said (b), and said (c) with another finely divided metal selected from the group consisting of aluminum, beryllium, and lithium, and mixtures thereof; the total amount of said oxidizer, said catalyst, and said finely divided metal in said composition not exceeding 96.5 parts by weight.

The finely divided high energy additives suitable for use in the practice of the invention include boron, magnesium, mixtures of boron and magnesium, and mixtures of boron and/or magnesium with another finely divided element such as aluminum, beryllium and lithium. When mixtures of boron and/or magnesium together with, said aluminum, beryllium and lithium are employed, the boron and/or magnesium is present in said mixture in an amount equal to at least 50 weight percent of said mixture. The amount of said high energy additive employed in the propellant compositions of the invention is usually within the range of 1 to 10 parts by weight based on the total propellant composition.

It is preferred that said finely divided high energy additives have a particle size less than 50 microns, more preferably less than 20 microns, and still more preferably less than 10 microns.

As mentioned above, ammonium nitrate is the oxidizer component employed in the propellant compositions of the invention. When said propellant compositions contain more than 88 weight percent of ammonium nitrate it is preferred to use a phase-stabilized ammonium nitrate. One method of phase stabilizing ammonium nitrate is to admix about 10 parts of a potassium salt (usually potassium nitrate) with about 90 parts of ammonium nitrate, along with some water, heat the mixture to about 140° F., dry, and then grind to the desired particle size. The desired particle size for the oxidizer component employed in the propellants of the invention is preferably within the range of 20 to 250 microns. The amount of oxidizer component employed in the propellant compositions of the invention is from 86 to 94 parts by weight based on the total composition.

The term "rubbery polymer" as used herein and in the claims, unless otherwise specified, includes natural rubber and all rubbery polymers of olefins and diolefin which are prepared by either emulsion polymerization or mass 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.

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A presently preferred rubbery polymer is a copolymer of 1,3-butadiene with 2-methyl-5-vinyl pyridine.

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 40. 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.

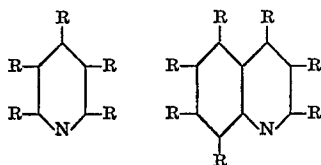
Instead of using a single conjugated diene, a mixture of conjugated dienes can be employed. Thus, a mixture of 1,3-butadiene and isoprene can be employed as the conjugated diene portion of the monomer system.

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,

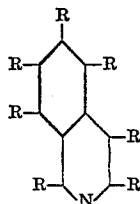


substituent wherein R' is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl (isopropenyl) group. Of these, the compounds of the pyridine series are of the greatest interest commercially at present. Various substituted derivatives are also applicable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



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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-ethoxy-pyridine; 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-din-propylquinoline; 2-methyl-4-nonyl-6-vinylpyridine; 4-(alpha-methylvinyl)-8-dodecylquinoline; 3-vinylisoquinoline; 1,6-dimethyl-3-vinyl-isoquinoline; 2-vinyl-4-benzylquinoline; 3-vinyl-5-chloroethylquinolein-3-vinyl-5,6-dichloroisoquinoline; 2-vinyl-6-ethoxy-7-methylquinoline; 3-vinyl-6-hydroxymethylisoquinoline; and the like.

Another preferred 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 4 to 8 parts by weight based on the total propellant composition.

The copolymer comprising a conjugated diene and a polymerizable heterocyclic nitrogen base can also be cured by a quaternization reaction by incorporating therein a quaternizing agent and subjecting the resulting mixture to quaternizing conditions of temperature. Suitable quaternizing agents include alkyl halides such as methyl

iodide, methyl bromide; alkylene halides such as methylene iodide, ethylene bromide; substituted alkanes such as chloroform, bromoform, alkyl sulfates such as methyl sulfate; and various substituted aromatic compounds such as benzoyl chloride, methyl benzene sulfonate, benzo-trichloride, benzyl chloride, benzal chloride, hexachloro-p-xylene, and the like.

The quaternizing temperature is usually in the range zero to 250° F., although temperatures outside this range can be used.

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

	Parts by weight
Rubbery polymer.....	100
Reinforcing agent.....	0-50
Plasticizer	0-100
Wetting agent.....	0-10
Antioxidant	0-3
Vulcanization accelerator.....	0-5
Sulfur	0-2
Quaternizing agent.....	0-25
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), Paraflex (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.

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

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

Examples of vulcanization accelerators are those of the carbamate type, such as N,N-dimethyl-S-tert-butylsulfenyl dithiocarbamate and Butyl-Eight. Butyl-Eight is a rubber accelerator of the dithiocarbamate type 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 mixture of plasticizers rather than a single material.

The propellant compositions of the invention will preferably contain, in addition to the oxidizer component, the binder component, and the high energy additive component, a burning rate catalyst. Any suitable burning rate catalyst can be used in the propellant compositions of the invention. It is preferred that the burning rate catalyst be as finely divided as possible, preferably having a particle size of less than 20 microns. Burning rate catalysts applicable in the practice of the invention include

ammonium dichromate, iron oxide, copper chromite, Milori blue, and the like. Metal ferrocyanides and ferricyanides can also be used. Ferric ferrocyanides, such as Prussian, Berlin, Hamburg, Chinese, Paris and Miliori blue (mentioned above), soluble ferric ferrocyanide such as soluble Berlin or Prussian blue which contains potassium ferric ferrocyanide and ferric ferrocyanide which has been treated with ammonia, are among the materials which can also be used. Ferrous ferricyanide (Turnbull's blue) is also applicable. Milori blue, mentioned above, is a pigment similar to Prussian blue but having a red tint and is prepared by the oxidation of a paste of potassium ferrocyanide and ferrous sulfate. Other metal compounds such as nickel and copper ferrocyanides can also be employed. The amount of burning rate catalyst used in the propellant compositions of the invention can be within the range of 0 to 5 parts by weight based on the total composition.

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

	Parts by weight
Binder component.....	3.5-8
Oxidizer component.....	86-94
High energy additive.....	1-10
Burning rate catalyst.....	0-5

wherein the total of said oxidizer, said high energy additive, and said catalyst does not exceed 96.5 parts by weight of the total composition.

The various ingredients in the propellant composition can be mixed in any suitable manner on a roll mill or an internal mixer such as a Banbury, or a Baker-Perkins dispersion blade mixer can be employed. Any other suitable type of mixing device can be employed. The binder forms a continuous phase in the propellant with the oxidant as the discontinuous phase. One procedure for blending the propellant ingredients utilizes a stepwise or incremental incorporation of the oxidant ingredient and other "dry" ingredients into the binder component. The binder ingredients are mixed to form a binder mixture and the oxidizer ingredient, together with the high energy additive, the burning rate catalyst (if one is used), and any other "dry" ingredients, are then added to said binder mixture in subsequent incremental additions.

Another method of mixing the ingredients of the propellant composition comprises a solvent mixing technique. In this method the rubbery polymer, or the binder component, is dissolved in an excess of a suitable solvent to form a solution. The other components of the propellant composition such as the oxidant component and the burning rate catalyst are then incorporated into said solution. After said other ingredients are thoroughly dispersed, heat and vacuum are applied to remove the excess solvent. Constant mixing is usually carried out during the application of heat and vacuum to remove said solvent.

Examples of suitable solvents which can be employed in said solvent mixing technique are normal hexane, cyclohexane, benzene, toluene, methylcyclohexane, normal heptane, o-xylene, m-xylene and ethylbenzene.

After the propellant compositions have been formulated by one of the above mixing techniques the compositions can be compression molded into any desired shape or configuration. Molding pressures within the range of 3,000 to 20,000 p.s.i. are normally employed although higher molding pressures can be employed if desired. The preferred molding pressure is usually in the range of 8,000 to 12,000 p.s.i. The molding can be carried out at any temperature between atmospheric temperature and 220° F. Atmospheric temperatures, e.g., about 70 to about 80° F. are preferred.

The flow properties of the propellant compositions of the invention having the described high oxidizer contents are such that said compositions cannot be extruded by conventional methods. I have found that said propellant compositions can be extruded in conventional extrusion

apparatus by incorporating an extrusion aid in the propellant composition. I have found that highly halogenated compounds can be employed as extrusion aids in solid composite propellant compositions. The polymers and copolymers of highly halogenated olefins containing from 2 to 4 carbon atoms per molecule and an average of from 1 to 2 halogen atoms per atom of carbon, are particularly useful as extrusion aids. Said polymers can be prepared by polymerizing said olefins at temperatures of about 70 to about 200° C. in the presence of peroxide promoters such as benzoyl peroxide and acetyl peroxide. Methods for the preparation of said polymers are well known to those skilled in the art. Further details regarding the preparation of said polymers can be found in Belmore et al., "Production of Polyperfluorovinyl Chloride," Industrial Engineering Chemistry, 39, 338-342 (1947) and in U.S. Patents 2,694,701 issued to Oscar A. Blum et al. on November 16, 1954, 2,784,176 issued to A. L. Dittman on March 5, 1957, and 2,705,706 issued to A. L. Dittman et al., on April 5, 1955.

Examples of said polymers include, among others, the polymers of: trifluorochloroethylene (Kel-F polymer oil); tetrafluoroethylene; perfluorobutadiene; difluorodichloroethylene, including both $\text{CF}_2=\text{CCl}_2$ and $\text{CFCl}=\text{CFCl}$; perfluoropropene; perfluoromonochloroprene; perfluorobutene; and perfluoromonochlorobutene. Examples of said copolymers are the copolymers of: trifluorochloroethylene with fluorochloroisobutene; trifluorochloroethylene with tetrafluoroethylene; trifluorochloroethylene with vinylidene fluoride; trifluorochloroethylene with vinyl fluoride; trifluorochloroethylene with vinyl chloride; trifluorochloroethylene with vinylidene chloride; trifluorochloroethylene with perfluoropropene; and trifluorochloroethylene with trifluorochloroethylene with trifluoroethylene.

Said highly halogenated compounds are usually used in the propellant compositions of the invention in amounts ranging from 0.1 to 2.0 weight percent of the total propellant composition.

The use of said highly halogenated compounds as processing aids in composite type propellants is further disclosed, and claimed, in my copending application, Serial No. 783,616, filed December 29, 1958.

The propellant compositions of the invention have good mechanical properties and good ballistic properties. Said compositions are useful as gas producers wherever high burning rate is desired. Said propellant compositions have good strength without curing, although curing can be employed if desired, for example, 24 hours at 180° F. The curing temperature will generally be in the range of 70 to 250° F., preferably between 140 and 200° F. The curing time must be long enough to give the desired mechanical properties in the propellant. The time will generally range from around 3 hours when a higher curing temperature is employed to about 28 days when curing is effected at lower temperatures.

The following examples will serve to further illustrate the invention.

EXAMPLE I

Two propellant compositions were formulated which contained 90/10 butadiene-styrene copolymer and phase-stabilized ammonium nitrate. The phase-stabilized ammonium nitrate was prepared by admixing 90 parts by weight ammonium nitrate and 10 parts by weight potassium nitrate with some water, heating the mixture to about 140° F., drying, and then grinding to approximately 40 micron particle size. The copolymer was prepared by emulsion polymerization and was masterbatched with a fast extruding furnace carbon black in a manner such as to provide a material containing 20 parts of carbon black per 100 parts of rubber as described in Example II. In one of these formulations anhydrous boron of approximately 1.0 micron particle size was employed. The propellant formulations, each containing burning

rate catalyst, were prepared by mixing the components together in a Baker-Perkins mixer. The compositions of the final propellants were as follows:

Components	Propellant A,	Propellant B,
	Parts by wt.	Parts by wt.
Binder (copolymer).....	8.0	8.0
NH_4NO_3 (stabilized).....	92.0	90.0
Ammonium dichromate (catalyst).....	2.0	2.0
Boron.....	0.0	2.0
Total.....	102.0	102.0

The individual propellant compositions were then pressed into strands at room temperature and 10,000 p.s.i. pressure, using a 10 minute press time. The strands were not cured. The strands after trimming to $\frac{3}{16}$ " diameter by 5" long, were burned in a standard strand bomb for the determination of burning rate. The results of these tests are given below in Table I.

Table I

Propellant	Test Temp., ° F.	Burning Rate	
		At 600 p.s.i. (in./sec.)	At 1,000 p.s.i. (in./sec.)
A.....	73	0.119	0.158
B.....	73	0.192	0.275

EXAMPLE II

A number of propellants were formulated by the method of Example I. The binder used in these runs was a 90/10 butadiene-2-methyl-5-vinylpyridine copolymer which had been prepared by emulsion polymerization according to the following recipe.

POLYMERIZATION RECIPE

Ingredient	Parts by weight
1,3-butadiene.....	90
2-methyl-5-vinylpyridine.....	10
Water.....	200
Potassium soap (office synthetic rubber).....	6
Potassium chloride.....	0.1
Sodium salt of condensed alkylaryl sulfonic acid.....	0.3
Tetrasodium salt of ethylenediaminetetraacetic acid.....	0.005
Tertiary-dodecyl mercaptan (modifier).....	(1)
Ferrous sulfate heptahydrate.....	0.2
Potassium pyrophosphate.....	0.253
Para-menthane hydroperoxide.....	0.135
Shortstop-potassium dimethyldithiocarbonate.....	0.15
Stabilizer-phenyl-B-naphthylamine.....	1.75

¹ A number of polymerization runs were made, after which the resulting polymer was blended together. The amount of modifier used in each run was in the range between 0.6 and 0.8 part by weight.

The latex, before coagulation, was masterbatched with a fast extruding carbon black in a manner to provide a material containing 20 parts of carbon black per 100 parts of rubber. The black masterbatch was then acid coagulated, washed with water, and dried.

After drying, 1.25 parts per 100 parts of rubber of a physical mixture containing 65% of a complex diarylamine-ketone reaction product and 35% of N,N'-diphenyl-p-phenylenediamine was milled into the rubber. This increased the amount of stabilizer present to 3 parts/100 parts of rubber.

The propellants of these runs were formulated by the same method employed in Example I. The oxidizer employed was identical to the phase-stabilized NH_4NO_3 of Example I. These propellants were formulated according to the following recipes.

Components	Propellant Compositions—Parts by Wt.								
	Propellants								
	C	D	E	F	G	H	J	K	L
Binder.....	6.0	6.0	6.0	4.0	6.0	6.0	6.0	6.0	6.0
Ammonium nitrate (stabilized).....	92.0	90.0	88.0	90.0	90.0	90.0	90.0	90.0	94.0
Ammonium dichromate (catalyst).....	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Boron (1.0 micron size).....	2.0	4.0	6.0	6.0	0.0	2.0	0.0	0.0	0.0
Magnesium (6-10 micron size).....	0.0	0.0	0.0	0.0	4.0	3.0	0.0	0.0	0.0
Magnesium-aluminum alloy ¹	0.0	0.0	0.0	0.0	0.0	0.0	4.0	0.0	0.0
Aluminum.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	0.0
Total.....	102.0	102.0	102.0	102.0	102.0	103.0	102.0	102.0	102.0

¹ 60% by weight magnesium—40% by weight aluminum.

The above propellants were burned in a strand bomb as in Example I to determine their burning rate. The burning rates are given below in Table II.

Table II

Propellant	Burning rate at 600 p.s.i. (inches/sec.)	Burning rate at 1,000 p.s.i. (inches/sec.)
C.....	0.196	0.290
D.....	0.240	0.348
E.....	0.271	0.382
F.....	0.292	0.415
G.....	0.216	0.300
H.....	0.262	0.390
J.....	0.176	0.248
K.....	0.138	0.201
L.....	0.146	0.203

In addition to the burning rate determination, several of the propellants given above were compression molded into small tubular grains, 3" O.D. x 1½" I.D. x 5" long and fired in a small rocket motor (static test). The results of several of these tests are given below in Table III.

Table III

Propellant	Temp., ° F.	Characteristic exhaust Velocity (ft./sec.) C*	At 600 p.s.i.		At 1,000 p.s.i.	
			Pressure exponent in $r = aP_c^n$	Burning rate at 600 p.s.i. (in./sec.)	Burning rate at 1,000 p.s.i. (in./sec.)	Pressure exponent in $r = aP_c^n$
C.....	73	4,608	0.07	0.204	0.299	0.76
D.....	73	4,671	0.65	0.250	0.360	0.71
E.....	73	4,675	0.65	0.263	0.372	0.67
F.....	73	4,642	0.70	0.287	0.412	0.69
G.....	73	4,522	0.60	not meas.	0.316	0.71
H.....	70	4,641	0.71	0.266	0.397	0.78
J.....	73	4,476	0.62	0.182	0.264	0.73

In the above runs given in Tables II and III, propellants C thru J represent propellants within the scope of the invention, propellant K demonstrates the ineffectiveness of aluminum alone as a high energy additive, and propellant L is a control run in which no high energy additive was employed. In the formula $r = aP_c^n$ given above, r = burning rate, a = a constant, P_c = chamber pressure.

EXAMPLE III

A run was made in which a propellant composition of low ammonium nitrate content containing boron metal was formulated and burned in a strand bomb. A control propellant containing no boron was prepared and run

for comparison. The binder component used had the following composition:

BINDER COMPONENT

	Parts by weight
Butadiene-MVP copolymer (90/10).....	100
25 Fast extruding carbon black.....	20
Benzophenone.....	20
Philcure ¹	1.00
Sulfur.....	0.75
Zinc oxide.....	3.00
30 Flexamine ²	3.00

¹ N,N-dimethyl-s-tert-butylsulfenyl dithiocarbamate.
² A physical mixture containing 65 weight percent of a complex diarylamine-ketone reaction product and 35 weight percent of N,N'-diphenyl-p-phenylenediamine.

The copolymer used in said binder component was identical with that of Example II except that the additional 1.25 parts of stabilizer incorporated after drying of the latex was not added. The carbon black was master-batched therewith as in Example II. Said binder component was prepared by adding the benzophenone, the

zinc oxide, the sulfur, and the Flexamine to said copolymer in a Baker-Perkins mixer and thoroughly incorporating said ingredients in said copolymer.

Two propellants having the following composition was then prepared.

PROPELLANT COMPOSITIONS, PARTS BY WEIGHT

	O	P
Binder.....	17.5	17.5
Ammonium nitrate.....	82.5	82.5
Ammonium dichromate.....	4.0	4.0
Boron.....	0.0	4.0

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Said propellant P was prepared by first incorporating the boron into said binder component in the Baker-Perkins mixer. The ammonium dichromate and the ammonium nitrate were dry-blended together and the resulting dry-blend was incorporated into the material in the mixer. Propellant O was prepared in the same manner except that the boron was omitted.

After all the ingredients had been thoroughly admixed, portions of the propellant compositions thus formed were extruded into strands which were cured for 24 hours at 180° F. The results of burning rate tests on said strands are given below.

BURNING RATE TESTS

Propellant	Burning Rate at 600 p.s.i. (in./sec.)	Burning Rate at 1,000 p.s.i. (in./sec.)	Pressure Exponent-n
O.....	0.147	0.201	0.61
P.....	0.127	0.184	0.71

The above data demonstrate that for a composition low in ammonium nitrate, the addition of boron is actually detrimental to the burning rate and the burning rate exponent.

EXAMPLE IV

A run was made in which an extrudable propellant composition of high ammonium nitrate content containing boron and magnesium was formulated and burned in a strand bomb. A control propellant containing no boron or magnesium was prepared and run for comparison. The binder component used had the following composition:

BINDER COMPONENT

	Parts by weight
Butadiene-MVP copolymer (90/10).....	100
Fast extruding carbon black.....	22
Flexamine.....	3
Butarez-25 ¹	48

¹ Butarez-25 is a liquid polybutadiene, prepared by sodium-catalyzed polymerization in heptane and having a Saybolt Furol viscosity (SFS) at 100° F. of approximately 2500 seconds. Further details regarding the preparation of said Butarez-25 and other suitable liquid polybutadienes can be found in Patent 2,631,175 issued March 10, 1953 to W. W. Crouch.

The copolymer used in said binder component was the same as that used in Example II except (1) the additional 1.25 parts of stabilizer incorporated after drying of the latex was not added, and (2) an additional 2 parts of carbon black was masterbatched therewith to give a total of 22 parts of carbon black per 100 parts of copolymer. Said binder component was prepared by adding the Butarez-25 and Flexamine to said copolymer in a Baker-Perkins mixer and thoroughly incorporating same in said copolymer.

Two propellants having the following composition were prepared using said binder component.

PROPELLANT COMPOSITIONS, PARTS BY WEIGHT

	R	S
Binder.....	7	7
Ammonium nitrate (stab.).....	91	88
Ammonium Dichromate.....	1	0.5
Kel F Polymer Oil (#1).....	1	0.5
Boron (0.8-1.0 micron).....	0	2.0
Magnesium (13-22 micron).....	0	2.0

Said propellant S was prepared by first mixing the Kel F polymer oil with the ammonium nitrate in a Baker-Perkins mixer. The boron, the magnesium, and the ammonium dichromate were incorporated into said binder component after which the Kel F polymer oil-ammonium nitrate mixture was incorporated into said binder component in increments with complete incorporation after addition of each increment. Said propellant

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R was prepared in the same manner except that the boron and magnesium were omitted.

After all the ingredients had been thoroughly admixed the propellant compositions thus formed were extruded into strands and burning rate tests were run on said strands. The results of said burning rate tests are given below.

BURNING RATE TESTS

Propellant	Burning Rate at 600 p.s.i. (in./sec.)	Burning Rate at 1,000 p.s.i. (in./sec.)	Pressure Exponent-n
R.....	0.115	0.224	0.7
S.....	0.224	0.343	0.51

As will be noted, burning rate and burning rate exponent are favorably affected by the presence of the high energy additives boron and magnesium.

Another portion of said propellant S was compression molded at 8000-10,000 pounds' pressure into tubular grains 5" long x 3" O.D. x 1½" I.D. These grains were then fired in a static test motor and the following results were obtained. These results are given below.

Test Temp., ° F.	Characteristic Exhaust Velocity O* (ft./sec.)	Burning rate at 600 p.s.i. (in./sec.)	Burning rate at 1,000 p.s.i. (in./sec.)	Specific Impulse at 1,000 p.s.i., seconds
FIRED IMMEDIATELY AFTER FORMATION				
75.....	4,590	0.202	0.292	210
FIRED AFTER 3 MONTHS' STORAGE AT 170° F.				
75.....	4,310	0.207	0.297	214
FIRED AFTER 6 MONTHS' STORAGE AT 170° F.				
75.....	4,495	0.206	0.296	209

The strand burning test reported in the above examples were determined on strands which were approximately 3/16" in diameter and having surfaces thereof except one end restricted so as to prevent burning on said one end. In carrying out said tests the strands were placed in a pressure bomb and the bomb was pressured to the desired pressure with nitrogen. The bomb was then placed in a temperature bath maintained at 75° F. The strands were then ignited and the time required for the propellant to burn between two fusible wires spaced a measured distance apart was recorded. The burning rate was then calculated in inches per second.

The propellant compositions of the present invention can be used in any of the known utilities for propellants, for example, rocket engines, takeoff assist units, gas generators and the like. The propellant compositions of the present invention are particularly applicable where it is desired to utilize a propellant in which ammonium nitrate is the oxidizer and wherein it is desired to obtain a near stoichiometric ratio of oxidizer to fuel.

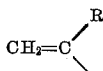
As will be evident to those skilled in the art various modifications of the invention can be made or followed in the light of the above disclosure without departing from the spirit or scope of the invention.

We claim:

1. A solid propellant composition consisting essentially of, in parts by weight per 100 parts of the total composition: from 3.5 to 8 parts of a binder component comprising a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of a conjugated diene containing from 4 to 10 carbon atoms per molecule and styrene, and co-

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polymers of a conjugated diene containing from 4 to 10 carbon atoms per molecule and a



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 hydrogen and a methyl radical; from 86 to 94 parts of an ammonium nitrate oxidizer component; from 0 to 5 parts of a suitable burning rate catalyst; and from 1 to 10 parts of a finely divided high energy additive selected from the group consisting of boron and mixtures of boron and magnesium containing at least 50 weight percent boron; the total amount of said oxidizer, said catalyst, and said finely divided high energy additive in said composition not exceeding 96.5 parts by weight.

2. A propellant composition according to claim 1 wherein the particle size of said finely divided high energy additive is less than 50 microns.

3. A propellant composition according to claim 1 wherein the particle size of said finely divided high energy additive is less than 20 microns.

4. A propellant composition according to claim 1 wherein the particle size of said finely divided high energy additive is less than 10 microns.

5. A propellant composition according to claim 1 wherein said finely divided high energy additive is boron.

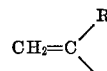
6. A propellant composition according to claim 1 wherein said finely divided high energy additive is a mixture consisting essentially of boron and magnesium.

7. A propellant composition according to claim 1 wherein said ammonium nitrate oxidizer component is a phase stabilized ammonium nitrate.

8. A propellant composition according to claim 1 wherein said rubbery polymer of said binder component

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is a copolymer of (a) a conjugated diene containing from 4 to 10 carbon atoms per molecule and (b) a



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 hydrogen and a methyl radical.

9. A propellant composition according to claim 8 wherein said copolymer is a copolymer of 1,3-butadiene and 2-methyl-5-vinylpyridine, said ammonium nitrate is phase stabilized, and said high energy additive is a mixture of boron and magnesium.

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