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COMPOSITE PROPELLANT REINFORCED WITH NITROGEN COMPOUNDS

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This invention relates to composite type propellants. In one aspect this invention relates to composite type propellants suitable for use in rocket motors and in guns.

In recent years, considerable work has been directed toward the development of solid propellants suitable for use in rocket motors. Rockets employing solid propellant fuels are extensively used by the military and have also achieved considerable importance in commercial operations. For example, solid rocket propellants are utilized in missiles, projectiles, and rockets to assist planes in take-off or to furnish an extra surge of power in flight. A solid propellant to be satisfactory for its intended use should possess certain desirable physical characteristics. For example, the propellant should have the required tensile strength and the required modulus of elasticity. Furthermore, it would be especially desirable to provide a propellant which can be readily adapted without exhaustive tests to form slow, intermediate, or fast burning rocket grains. Ammonium nitrate was long considered to be unsuitable as an ingredient in propellant compositions because of lack of a suitable binder or fuel component which would permit incorporation of sufficient ammonium nitrate to provide near the theoretical stoichiometric amount of oxygen necessary to burn said binder or fuel component.

Recently, superior solid propellant materials have been discovered which comprise a solid oxidant, such as ammonium nitrate or ammonium perchlorate and a rubber 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. These new propellants have been highly successful in rocket motors.

This invention is particularly applicable to propellants of the type described in the preceding paragraph. In such propellant compositions it has been customary to utilize carbon black as a reinforcing agent. Said carbon black requires large amounts of oxygen for complete combustion to carbon dioxide. When less than the stoichiometric amount of oxygen is present a considerable amount of carbon monoxide is found in the combustion gases. Said carbon monoxide is highly undesirable from a military standpoint because upon reaching the atmosphere, as at the muzzle of a gun, after-burning or flash occurs. A deficiency of oxygen also results in the formation of large quantities of smoke. This is also objectionable from a military standpoint because smoke or flash can reveal the location of the gun or ship to the enemy.

These difficulties can be mitigated by replacing a portion or all of the carbon black in the propellant with a high nitrogen content material as the reinforcing agent. By thus replacing the carbon black, the main objections to the above-described propellants, i.e., flash and formation of smoke, are largely eliminated because the oxygen deficiency has been decreased. The new propellants of the invention also possess other advantages which are discussed hereinafter. Thus, broadly speaking, the present invention resides in the improvement of using a high nitrogen content material as at least a portion of the reinforcing agent in propellant compositions comprising a solid

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oxidant and a polymeric material. In one embodiment of the invention a high oxygen content plasticizer is also employed to further decrease the oxygen deficiency.

An object of this invention is to provide an improved propellant suitable for use in guns and in rocket motors. Another object of this invention is to provide an improved propellant suitable for use in guns and in rocket motors, which propellant is easily processed and less costly. Still another object of this invention is to provide an improved propellant comprising a solid inorganic oxidizer and a rubbery copolymer binder or fuel component in which a near theoretical stoichiometric oxygen balance is obtained. Still another object of this invention is to provide an improved propellant having a reduced carbon content. Another object of this invention is to provide an improved propellant having reduced flash and smoke producing properties. A further object of this invention is to provide an improved propellant which causes less erosion and/or corrosion to gun barrels. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

Thus according to the invention, there is provided a solid propellant composition comprising a major portion of a solid inorganic oxidizing salt as an oxidizer component and a minor portion of a copolymer of a conjugated diene with a heterocyclic nitrogen base as the binder component. In said binder component, at least a portion of the customarily employed carbon black reinforcing agent is replaced with a high nitrogen content compound containing at least 30 weight percent of nitrogen and having a sensitivity to impact of at least 15 as measured by the Bureau of Mines impact test.

In one embodiment of the invention a high oxygen content material containing at least 30 percent by weight of oxygen is used as a plasticizer in the propellant composition along with the high nitrogen content material.

Sensitivity to impact is determined by subjecting a small quantity of confined explosive to the transmitted shock from a falling weight—usually 2 kg.—and determining the minimum height of fall that will cause at least one explosion in ten tests. In the Bureau of Mines test, 0.02 gram of the material to be tested is spread evenly over an area 1 cm. in diameter and confined by means of a plunger having a tip 1 cm. in diameter. The falling 2 kg. weight strikes the upper end of the plunger. If the explosive is liquid, the sample is held in position by being absorbed in a disk of dried filter paper 1 cm. in diameter. Thus herein and in the claims the sensitivity to impact of at least 15 refers to the minimum height of fall of the 2 kg. weight which will cause at least one explosion in ten tests conducted according to the above described Bureau of Mines test.

The high nitrogen content material employed as a reinforcing agent in the invention is a solid material containing at least 30 weight percent nitrogen, usually from 30–83 weight percent nitrogen. Certain high nitrogen content materials are extremely sensitive to shock and are classified as primary explosives or initiators. Such materials, while they would probably be satisfactory reinforcing agents, cannot be readily and safely incorporated in propellant compositions when employing presently known processing or mixing techniques. Therefore, the preferred high nitrogen content materials of the invention are those which have a sensitivity to shock of at least 15 when measured by the Bureau of Mines impact test.

The high nitrogen content reinforcing agents must also be compatible on a chemical and physical basis with the other propellant ingredients. As will be realized by those skilled in the art compatibility can be determined in a number of ways. The particular method employed for determining compatibility for any specific high nitrogen content reinforcing agent will depend upon the particular

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reinforcing agent, the other ingredients in the propellant, and the degree of stability required. One method for determining chemical stability or compatibility which has been found useful in many instances is the standard Picatinny Arsenal 90° C. vacuum stability test. When tested according to this method the composite propellant of the invention containing the high nitrogen content reinforcing agent shall not explode and shall not give more than 10 milliliters of gas when five grams of the composite propellant are heated for a period of 40 hours. The chemical stability test is determined on freshly prepared propellant after cure and also on propellant which has been stored for two years at 50° C.

One method for determining physical stability or compatibility is according to a standard test developed by Picatinny Arsenal. In this test, propellant grains after two years storage at 65.5° C. shall give compression values that are at least equal to 50 percent of the compression value obtained on unstored, i.e., original or newly prepared propellant grains.

Any other suitable method for determining chemical compatibility and physical compatibility can be employed.

High nitrogen content materials applicable in the practice of the invention include, among others, the following: melamine, oxamide, RDX (1,3,5-trinitro-1,3,5-triazocyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane), ammonium picrate, ethylenedinitramine, trinitrotoluene, dicyandiamide, urea, and hydrazine nitrate.

It is to be noted that some of the above-mentioned high nitrogen content materials also have a high oxygen content. The oxygen content in these materials would be available to further decrease the oxygen deficiency of the propellant. However, such materials are not necessarily the most preferred reinforcing agents. Although the carbon black reinforcing agents of the prior art are usually superfine (less than 0.1 micron particle size) the range of particle size for the high nitrogen content reinforcing agents of the invention can be from 0.03 to 50 microns. Usually a particle size of less than 10 microns is preferred because it tends to give more uniform ballistics. However, coarser particle sizes, at least in some amount, are advantageous in that they act as "cratering agents" and increase the burning rate of the gun propellants. Thus in some instances it is preferred to use a reinforcing agent having a range of particle sizes.

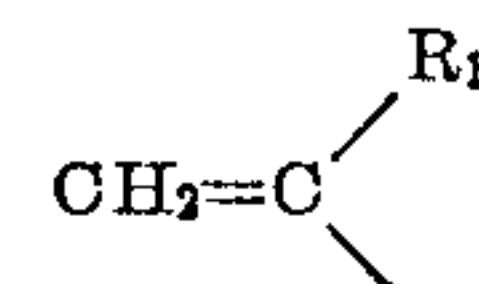
The rubbery polymers employed as binders in the solid propellant compositions of this invention are copolymers of conjugated dienes with polymerizable heterocyclic nitrogen bases of the pyridine series. These copolymers can vary in consistency from very soft rubbers, i.e., materials which are soft at 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 4 to 8 carbon atoms per molecule and include 1,3-butadiene, isoprene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-methoxybutadiene, 2-phenylbutadiene, 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 in the preparation of the polymeric binders

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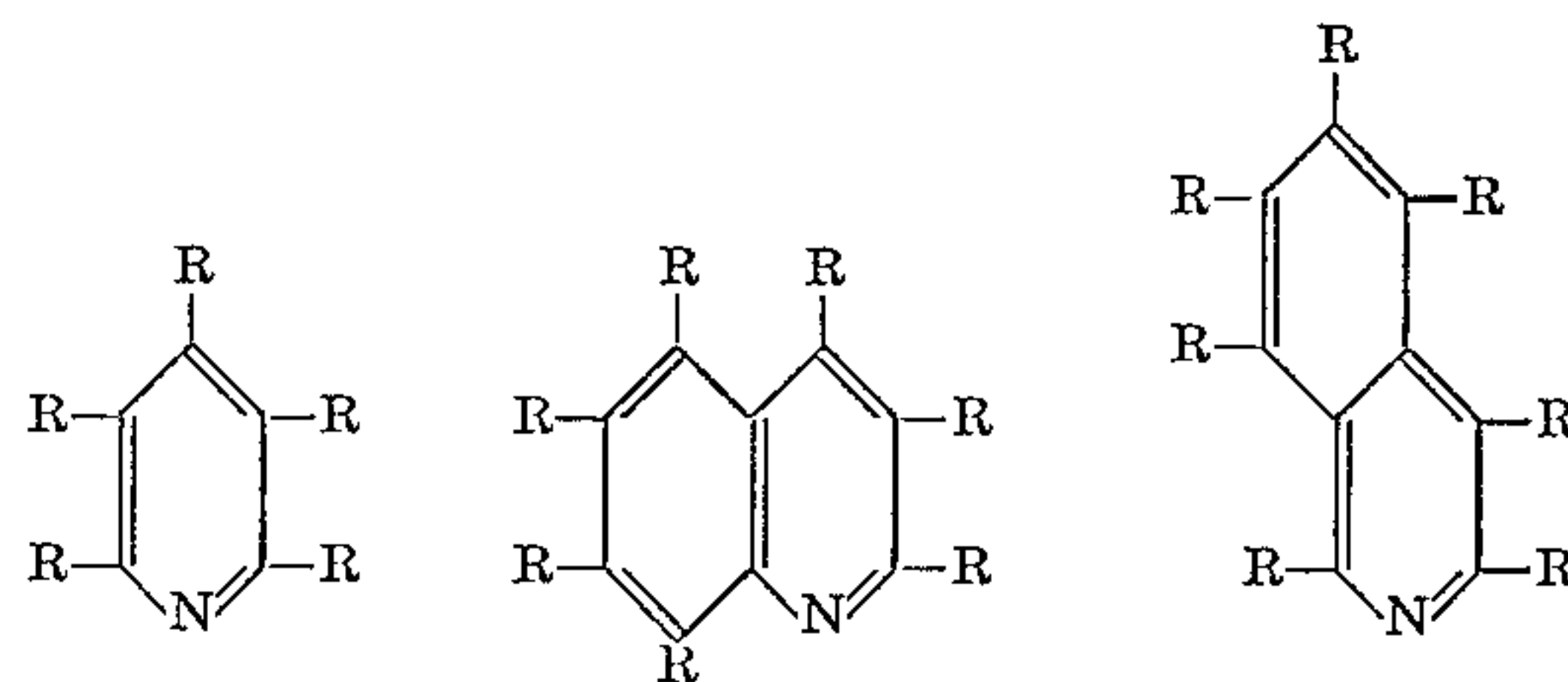
of this invention. Furthermore, instead of using a single conjugated diene, a mixture of conjugated dienes can be employed. Thus, a mixture of 1,3-butadiene and isoprene can be employed as the conjugated diene portion of the monomer system.

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 R₁ 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 at present of the greatest interest commercially. Various substituted derivatives are also applicable but the total number of carbon atoms in the groups attached to the carbon atoms of the heterocyclic nucleus should not be greater than 15 because the polymerization rate decreases somewhat with increasing size of the alkyl group. Compounds where the alkyl substituents are methyl and/or ethyl are available commercially.

These heterocyclic nitrogen bases have the formula



where R is selected from the group consisting of hydrogen, alkyl, vinyl, alpha-methylvinyl, alkoxy, halo, hydroxy, cyano, aryloxy, aryl, and combinations of these groups such as haloalkyl, alkylaryl, hydroxyaryl, and the like; one and only one of said groups being selected from the group consisting of vinyl and alpha-methylvinyl; and the total number of carbon atoms in the nuclear substituted groups being not greater than 15. Examples of such compounds are

- 2-vinylpyridine;
- 2-vinyl-5-ethylpyridine;
- 2-methyl-5-vinylpyridine;
- 4-vinylpyridine;
- 2,3,4-trimethyl-5-vinylpyridine;
- 3,4,5,6-tetramethyl-2-vinylpyridine;
- 3-ethyl-5-vinylpyridine;
- 2,6-diethyl-4-vinylpyridine;
- 2-isopropyl-4-nonyl-5-vinylpyridine;
- 2-methyl-5-undecyl-3-vinylpyridine;
- 2,4-dimethyl-5,6-dipentyl-3-vinylpyridine;
- 2-decyl-5-(alpha-methylvinyl)pyridine;
- 2-vinyl-3-methyl-5-ethylpyridine;
- 2-methoxy-4-chloro-6-vinylpyridine;
- 3-vinyl-5-ethoxypyridine;
- 2-vinyl-4,5-dichloropyridine;
- 2-(alpha-methylvinyl)-4-hydroxy-6-cyanopyridine;
- 2-vinyl-4-phenoxy-5-methylpyridine;
- 2-cyano-5-(alpha-methylvinyl)pyridine;
- 3-vinyl-5-phenylpyridine;
- 2-(para-methyl-phenyl)-3-vinyl-4-methylpyridine;
- 3-vinyl-5-(hydroxyphenyl)-pyridine;
- 2-vinylquinoline;
- 2-vinyl-4-ethylquinoline;
- 3-vinyl-6,7-di-n-propylquinoline;
- 2-methyl-4-nonyl-6-vinylquinoline;
- 4-(alpha-methylvinyl)-8-dodecylquinoline;
- 3-vinylisoquinoline;
- 1,6-dimethyl-3-vinylisoquinoline;
- 2-vinyl-4-benzylquinoline;

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3-vinyl-5-chloroethylquinoline;
 3-vinyl-5,6-dichloroisoquinoline;
 2-vinyl-6-ethoxy-7-methylquinoline;
 3-vinyl-6-hydroxymethylisoquinoline;

and the like.

Oxidants which are applicable in the solid propellant compositions of this invention include ammonium, alkali metal, and alkaline earth metal salts of nitric and perchloric acids, and mixtures thereof. Ammonium nitrate and ammonium perchlorate are the preferred oxidants for use in the solid rocket fuels of this invention. Specific oxidants include sodium nitrate, potassium perchlorate, calcium nitrate and barium perchlorate. Mixtures of oxidants are also applicable. In the preparation of the solid rocket propellant compositions, the oxidants are powdered to sizes preferably finer than 200 mesh. The amount of solid oxidant employed is usually a major amount of the total composition and is generally in the range between about 500 and about 1000 parts of oxidant per 100 parts of copolymer. However, it is preferred to use between 750 and 900 parts of oxidant per 100 parts of copolymer.

While numerous perchlorate salts have been included in the above named suitable oxidants, ammonium nitrate is usually preferred for gun propellants because when the perchlorates are burned the resulting hydrochloric acid is corrosive to the gun barrel. However, perchlorates can be used as the oxidants in gun propellants when corrosion and erosion resistant liners such as Stellite, or metal plated (as chromium) gun barrels are employed. In one embodiment of the invention a mixture of nitrate and perchlorate oxidizer is employed and the amount of perchlorate is limited to an amount such that the amount of hydrochloric acid formed upon decomposition of the perchlorate will be stoichiometrically equivalent to the amount of metal oxide such as magnesium oxide and/or zinc oxide present in the propellant composition.

The propellant composition, in addition to the binder and oxidant, can contain a suitable combustion or burning rate catalyst such as metal ferrocyanides and ferri-cyanides. Ferric ferrocyanides, such as Prussian, Berlin, Hamburg, Chinese, Paris, and milori blue, 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 be used. Ferrous ferri-cyanide, Turnbull's blue, is also applicable. A particularly effective burning rate catalyst is milori blue which 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 this invention is usually in the range of 0 to 30 parts per 100 parts of rubbery polymer with from 15 to 30 parts being most frequently preferred.

The binder contains rubber copolymer of the type hereinbefore described and in addition to the above described reinforcing agents, there may also be present plasticizers, wetting agents, antioxidants, burning rate catalyst, and other compounding ingredients. Thus 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 present in amounts insufficient to affect the novel characteristics of the propellant composition.

In general, any suitable 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 of 100° F. of about 2000 seconds), di-butoxyethoxyethyl formal, and dioctyl phthalate are suitable plasticizers. Materials which provide

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rubber having good low temperature properties are preferred.

While any suitable rubber plasticizer can be utilized in the practice of the invention as indicated above, it is preferred to use a high oxygen content material as a plasticizer so as to further decrease the oxygen deficiency of the propellants. Usually the high oxygen content plasticizer will contain from 30-45 weight percent of oxygen. Mixtures of the high oxygen content plasticizers together with the other above named plasticizers can also be used.

Examples of suitable high oxygen content plasticizers which can be used in the practice of the invention include, among others, the following: triacetin, triethylene glycol dinitrate, dibutyloxalate, dibutyltartrate, dinitroethylbenzene, dinitrotoluene, and diethylene glycol dinitrate. The high oxygen content materials should have a sensitivity to impact of not less than 15, and should also be compatible on a chemical and physical basis with the other ingredients of the propellant composition, as defined above in connection with the high nitrogen content materials.

Wetting agents aid in deflocculating or dispersing the oxidizer. Aerosol OT (dioctyl ester of sodium sulfosuccinic acid), lecithin, and Duomeen C Diacetate (reaction product of acetic acid with the mono-salt formed from trimethylene diamine and coconut oil acid) are among the materials which can be employed.

Antioxidants 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-methylenebis (4-methyl-6-tert-butylphenol), and the like. Rubber antioxidants, in general, may be employed, or, if desired, they may be omitted.

It is to be understood that each of the various types of compounding ingredients may be used singly or mixtures of various ingredients performing a certain function may be employed. For example, it is sometimes preferred to use mixtures of plasticizers rather than a single material. It is to be understood also that the various compounding ingredients perform other functions in the propellant composition as well as the principal function indicated by the terms used to describe the various ingredients.

A general formulation for a binder composition in accordance with the invention as described above is set forth below:

Ingredients	Parts per Hundred Parts of Copolymer
Copolymer.....	100
Carbon black and high nitrogen content material (total) ¹	10-50
Plasticizer.....	10-50
Combustion catalysts.....	0-30
Metal oxide.....	0-5
Antioxidant.....	0-5
Wetting agent.....	0-2
Accelerator.....	0-2
Curing agent.....	0-2

¹ Each can range from 10 to 50.

Incorporated into said binder composition will be the oxidizer component in the amount of 500-1000 parts per hundred parts of copolymer.

The various ingredients in the propellant composition can be mixed by any of the rubber processing techniques known to the prior art. In preparing the above described propellant compositions of the prior art the mixing is usually accomplished in mixers of the kneader type with vertically or horizontally mounted blades, such as the Baker-Perkins mixer, the Bramley Beken mixer, or in Banbury mixer (for relatively insensitive ammonium nitrate type propellants). It is desirable that said mixers be equipped with interchangeable attachments such as compression rams (mainly for relatively insensitive ammonium nitrate type propellants), vacuum heads, etc. A compression ram exerting considerable force on the ingredi-

ents can be advantageously applied during the mixing stages, particularly during the final mixing stage. Vacuum can be applied to remove entrained air or solvent when the solvent mixing technique is employed. When a carbon black is employed in the propellant compositions of the prior art it is usually masterbatched with the copolymer. Said masterbatching can be carried out in either the wet or dry state; the wet state is usually preferred. In one commonly used mixing procedure the binder ingredients are mixed in a Baker-Perkins mixer equipped with a dispersion blade. The copolymer, having the carbon black masterbatched therein, is kneaded alone for a short period and the remainder of the binder ingredients are then incorporated into said copolymer. The oxidizer ingredient is then added step-wise in four equal increments with sufficient kneading to completely incorporate one increment before another is added. Throughout said mixing, the compression ram can be employed as desired, depending on sensitivity of the propellant. The vacuum head is advantageously applied at the end of the mixing system to remove entrained air.

In mixing the propellant of the invention, the technique employed will vary depending upon whether or not the reinforcing agent which is being used to replace a portion or all of the carbon black reinforcing agent is sensitive or non-sensitive to shock. In those instances where the replacement reinforcing agent is non-sensitive, the mixing procedure can be the same as that described above for the propellants of the prior art. Whether or not the replacement reinforcing agent is masterbatched with the copolymer in the dry or wet state will depend upon the solubility of said reinforcing agent in water.

When shock-sensitive nitrogen containing materials are used as the replacement reinforcing reagent, the well-known solvent mixing technique can be employed if desired or necessary, depending upon compatibility of the ingredients and safety considerations. In said solvent mixing technique, a suitable solvent such as normal hexane, cyclohexane, benzene acetone, is used to dissolve the copolymer, and the remainder of the binder ingredients are then incorporated with the binder solution. The dry oxidizer component is then coated with said binder solution. Said coating is preferably carried out in a mixing vessel such as a Baker-Perkins or Bramley Beken mixer by adding increments of said oxidizer to said binder solution with sufficient agitation after each incremental addition to completely coat the particles of the oxidizer component. After complete incorporation of the oxidizer into said binder solution the excess solvent is removed by application of vacuum; agitation being continued during said removal of the solvent.

After removal of said solvent has been accomplished, and sufficient mixing of the components has occurred, the blended propellant is transferred to the extrusion or compression molding equipment. A presently preferred procedure is to extrude the propellant through suitable dieheads and cutting the perforated strands into grains with a McKernan-Terry propellant cutter equipped with a metal or graphite cutting die, the latter being employed with the more sensitive propellant compositions.

Alternately, and especially for relatively sensitive propellants or for the smaller granulations, the solvent type propellant mix may be blocked to remove air in conventional manner, followed by extrusion through suitable dies, cutting to size, and drying the granulated propellant simultaneously with the curing operation.

Sufficient curing of the solventless propellant grains will usually occur at room temperature, particularly when such materials as magnesium oxide and/or zinc oxide or GMF are included in the propellant composition. However, if it is desired to develop maximum physical properties, additional curing can be carried out at elevated temperatures. The curing temperature will be limited in some instances by the ingredients of the propellant composition but will generally be in the range of 70 to 250° F.; preferably between 170 and 200° F. The curing

time will depend upon the desired properties. Said time will generally range from around three hours when the higher curing temperatures are employed up to seven days when curing is effected at lower temperatures.

While this invention will be further described using a binder composition comprising a copolymer of a conjugated diene with a polymerizable heterocyclic nitrogen base of the pyridine series, such as vinylpyridine and various alkyl-substituted derivatives, it is to be understood that the corresponding quinoline and isoquinoline compounds are also applicable, i.e., vinylquinolines, vinyl-isoquinolines and various alkyl-substituted derivatives of these compounds.

The following Table I illustrates composite propellant compositions in accordance with the invention.

Table I

Composition	A		B		C	
	Wt. Per-cent	phr. ¹	Wt. Per-cent	phr. ¹	Wt. Per-cent	phr. ¹
Copolymer of 1,3-butadiene-2-methyl-5-vinylpyridine (90:10 Bd/MVP).....	9.96	100	9.96	100	9.96	100
Melamine, pulverized (in copolymer).....	1.76	17.6	1.76	17.6	1.76	17.6
ZP-211 (dibutylcarbitol-formal).....	1.97	19.8	1.97	19.8	1.97	19.8
Triacetin.....						
Flexamine (approx. 65% diarylamine ketone and 35% N,N' diphenylparaphenylene diamine).....	0.30	3.0	0.30	3.0	0.30	3.0
GMF ¹ (paraquinone di-oxime).....	0.21	2.1	0.21	2.1	0.21	2.1
MgO.....	0.50	5.0	0.50	5.0	0.50	5.0
ZnO.....	0.30	3.0	0.30	3.0	0.30	3.0
Ammonium nitrate.....	85.00	852	81.40	816	81.40	816
Ammonium perchlorate.....			3.60	36	3.60	36

NOTES.—To aid extrusion a few hundredths of a percent of candelilla wax may be added as a die lubricant.
¹ Parts per hundred parts of copolymer.

The following Table II illustrates typical single base service gun propellants.

Table II
M-6 PROPELLANT (ARMY)

Material	Percentage Composition by Weight		
	Ratio of Active Ingredients	Final Manufactured Grains	
		Minimum Volatile Solvent	Maximum Volatile Solvent
Nitrocellulose (13.15% N).....	87	84.84	82.69
Dinitrotoluene (DNT).....	10	9.75	9.50
Dibutylphthalate (DBP).....	3	2.93	2.85
Diphenylamine (DPA).....	1 (added)	0.98	0.96
Volatile solvent (mainly ethyl alcohol).....		1.00	3.50
Moisture (H ₂ O).....		0.50	.50
		100.00	100.00

NOTE.—For flash elimination potassium sulfate is added to certain granulations, usually 1.0±0.5 parts per hundred parts of propellant.

PYRO PROPELLANT (NAVY)

Material	Percentage Composition by Weight		
	Ratio of Active Ingredients	Final Manufactured Grains	
		Minimum Volatile Solvent	Maximum Volatile Solvent
Nitrocellulose, Pyro type (12.6% N).....	99	96.0	91.0
Diphenylamine.....	1	1.0	1.0
Volatile solvent (mainly ethyl alcohol).....		2.0	7.0
Moisture (H ₂ O).....		1.0	1.0

NOTE.—For flash elimination potassium sulfate is added to certain granulations, usually 1.0±0.5 parts per hundred parts of propellant.

The following Table III presents a comparison between properties of the composite propellant compositions of Table I and the conventional single base Army and Navy gun propellants of Table II.

Table III
PROPELLANT PROPERTIES

	Composite Propellant			Single Base Service Propellants	
	Compositions (Table I)				
	A	B	C	Army M6 ^a	Navy Pyro ^b
F, ft.-lb./lb. ^c	314*	318*	316*	310*±8*	313*±13*
Density, gm./cc.	1.59	1.60	1.60	1.575 ±0.01	1.606 ±0.02
T _v , °K. ^d	2,333	2,382	2,403	2,476 ±116	2,544 ±203
Percent N by weight	31.3	30.5	30.5	12.61 ±0.16	11.90 ±0.32
Theoretical oxygen balance (percent oxygen deficiency)	-7.7	-7.2	-5.9	-9.8 ±1.2	-5.7 ±2.6

^a Range of values based on minimum and maximum volatile solvent (ethyl alcohol) content of 1.0% and 3.5% with 0.50% external moisture.

^b Range of values based on minimum and maximum volatile solvent content of 2.0% and 7.0% with 1.0% external moisture.

^c Force or $F = nMRT_v$, where n = pound mols of gas, M = molecular weight, and R = gas constant.

^d Isochoric, adiabatic flame temperature at constant volume.

*000 omitted.

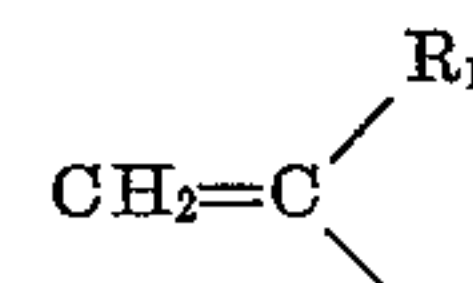
The above described Army M-6 propellant has a burning rate of 4.73 inches per second at 70° F. under 35,000 pounds per square inch pressure. The propellant compositions of the invention have a burning rate approximately ½ that of said Army propellant, depending upon the specific composition of the propellant. The lower burning rate of the composite propellants of the invention does not present any particular granulating problems because it is simply a matter of cutting the web size in half as compared to the web size of the Army M-6 propellant. The composite propellants of the invention can be extruded into multiple perforation grains or single perforated grains. The smaller web size for the composite propellants of the invention is advantageous in permitting higher loading densities in cartridge cases or bags, thereby permitting higher projectile velocities to be attained in guns which are designed for standard propellants.

The low material cost, per pound of propellant, for the composite propellants of the invention is only about one-third the material costs for the above-described Army M-6 and Navy Pyro propellants. Processing costs, particularly when no solvent is employed in mixing, are also considerably less because many of the usual operations for the preparation of the single base Army and Navy propellants, such as nitro cellulose dehydration, solvent recovery, water drying, and air drying are eliminated. In addition to being comprised of readily available low cost materials and propellants of the invention have high nitrogen contents (for example, those given in Table III contain about 31 weight percent nitrogen vs. about 12 weight percent for the existing single base propellants), have relatively low flame temperatures, and a generally improved oxygen balance. Said low flame temperature and high nitrogen content greatly increase the life of gun barrels and result in substantial elimination of flash, and production of less smoke due to improved oxygen balance.

Other advantages of the propellants of the invention will be apparent to those skilled in the art in view of the above disclosure. While the propellants of the invention have been described and illustrated with certain specific embodiments, the invention is not limited thereto. Various other modifications can be made, or followed, by those skilled in the art, in view of the above disclosure. Such modifications are believed to be within the spirit and scope of the invention.

I claim:

1. In a solid propellant composition consisting essentially of, in parts by weight per 100 parts by weight of a copolymer defined hereinafter, from 500 to 1000 parts of a solid inorganic oxidizing salt as an oxidizer component and 100 parts of a copolymer of (a) a conjugated diene containing from 4 to 8 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 R₁ is selected from the group consisting of hydrogen and a methyl radical, as a binder component, the improvement characterized by the presence in said composition of from 10 to 50 parts of a high nitrogen content compound selected from the group consisting of melamine, oxamid, RDX (1,3,5-trinitro - 1,3,5 - triazocyclohexane), HMX (1,3,5,7-tetranitro - 1,3,5,7 - tetrazocyclooctane), ammonium picrate, ethylenedinitramine, trinitrotoluene, dicyanidiamide, urea, and hydrazine nitrate, as at least a portion of the reinforcing agent in said binder component.

2. The propellant composition of claim 1 wherein said high nitrogen content compound is melamine.

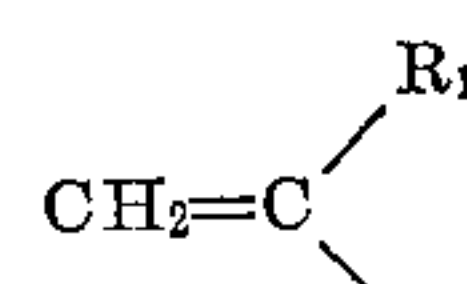
3. The propellant composition of claim 1 wherein said high nitrogen content compound is oxamide.

4. The propellant composition of claim 1 wherein said high nitrogen content compound is 1,3,5-trinitro-1,3,5-triazocyclohexane.

5. The propellant composition of claim 1 wherein said high nitrogen content compound is 1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane.

6. The propellant composition of claim 1 wherein said high nitrogen content compound is dicyandiamide.

7. A solid propellant composition consisting essentially of, in parts by weight per 100 parts of a copolymer defined hereinafter: from 500 to 1,000 parts of a solid inorganic oxidizing salt as an oxidizer component; and a binder component comprising 100 parts by weight of a copolymer of (a) a conjugated diene containing from 4 to 8 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 substituent is not more than 15 and wherein R₁ is selected from the group consisting of hydrogen and a methyl radical, from 10 to 50 parts of a high nitrogen content material selected from the group consisting of melamine, oxamid, RDX (1,3,5 - trinitro - 1,3,5-triazocyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane), ammonium picrate, ethylenedinitramine, trinitrotoluene, dicyanidiamide, urea, and hydrazine nitrate, and from 10 to 50 parts of a high oxygen content material selected from the group consisting of triacetin, triethyleneglycoldinitrate, dibutylxylate, dibutyltartrate, dinitroethylenebenzene, dinitrotoluene, and diethylenecycloclodinitrate.

8. The propellant composition of claim 7 wherein said high oxygen content compound is triacetin.

9. The propellant composition of claim 7 wherein said high oxygen content compound is diethyleneglycol dinitrate.

10. The propellant composition of claim 7 wherein said high oxygen content compound is triethyleneglycol dinitrate.

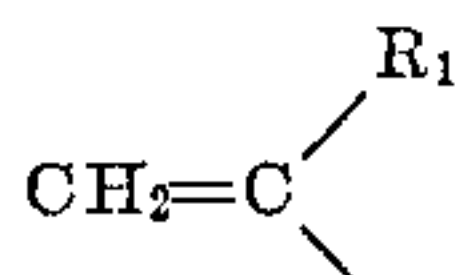
11. The propellant composition of claim 7 wherein said high oxygen content compound is dibutylxylate.

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12. The propellant composition of claim 7 wherein said high oxygen content compound is dibutyltartrate.

13. A propellant composition according to claim 7 wherein from 10 to 50 parts of carbon black are also present in said composition.

14. In a solid propellant composition consisting essentially of, in parts by weight per 100 parts of a copolymer defined hereinafter: from 500 to 1000 parts of a solid inorganic oxidizing salt as an oxidizer component; and as a binder component, 100 parts by weight of a copolymer of (a) a conjugated diene containing from 4 to 8 carbon atoms per molecule and (b) a



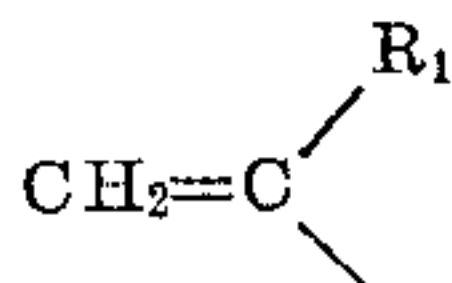
substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine, and alkyl substituted quinoline, wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15 and wherein R₁ is selected from the group consisting of hydrogen and a methyl radical; and from 10 to 50 parts of carbon black as a reinforcing agent; the improvement characterized by the presence in said composition of from 10 to 50 parts of a high nitrogen content material selected from the group consisting of melamine, oxamid, RDX (1,3,5-trinitro-1,3,5-triazocyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane), ammonium picrate, ethylenedinitramine, trinitrotoluene, dicyanidiamide, urea, and hydrazine nitrate.

15. The propellant composition of claim 14 wherein said solid inorganic oxidizer propellant is ammonium nitrate and said copolymer is a copolymer of 1,3-butadiene and 2-methyl-5-vinylpyridine.

16. The propellant composition of claim 14 wherein a portion of said solid inorganic oxidizer component is ammonium perchlorate and said copolymer is a copolymer of 1,3-butadiene and 2-methyl-5-vinylpyridine.

17. The propellant composition of claim 16 wherein said propellant also contains from 0 to 5 parts of a metal oxide selected from the group consisting of magnesium oxide, zinc oxide, and mixtures thereof, and wherein the amount of said ammonium perchlorate is an amount stoichiometrically equivalent to the amount of said metal oxide in said propellant composition.

18. A solid propellant composition consisting essentially of, in parts by weight per 100 parts of a copolymer defined hereinafter: as an oxidizer component, from 500 to 1000 parts of a solid inorganic oxidizing salt; as a binder component, 100 parts by weight of a copolymer of (a) a conjugated diene containing from 4 to 8 carbon atoms per molecule and (b) a

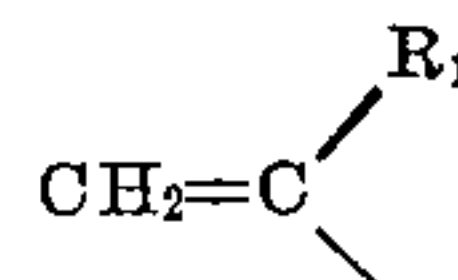


substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine and alkyl substituted quinoline, wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15 and wherein R₁ is selected from the group consisting of hydrogen and a methyl radical; as a reinforcing agent, from 10 to 50 parts of a high nitrogen content material, selected from the group consisting of melamine, oxamid, RDX (1,3,5-trinitro-1,3,5-triazocyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane), ammonium picrate, ethylenedinitramine, trinitrotoluene, dicyanidiamide, urea, and hydrazine nitrate; and as a plasticizing agent, from 10 to 50 parts of a high oxygen content material selected from the group consisting of triacetin, triethyleneglycoldinitrate, dibutyloxylate,

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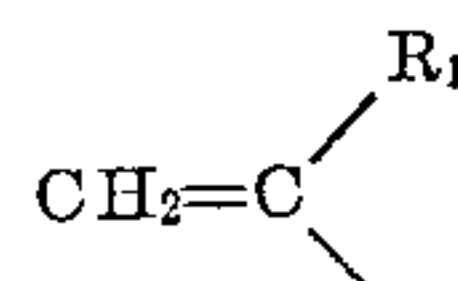
dibutyltartrate, dinitroethylbenzene, dinitrotoluene, and diethyleneglycoldinitrate.

19. A solid propellant comprising consisting essentially of, in parts by weight per 100 parts by weight of a copolymer defined hereinafter: from 500 to 1000 parts of a solid inorganic oxidizing salt as an oxidizer component; a binder component comprising 100 parts of a copolymer of (a) a conjugated diene containing from 4 to 8 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 R₁ is selected from the group consisting of hydrogen and a methyl radical; from 10 to 50 parts of a mixture of carbon black and a high nitrogen content compound selected from the group consisting of melamine, oxamid, RDX (1,3,5-trinitro-1,3,5-triazocyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane), ammonium picrate, ethylenedinitramine, trinitrotoluene, dicyanidiamide, urea, and hydrazine nitrate, as a reinforcing agent in said binder component; from 10 to 50 parts of a plasticizing agent in said binder component; and a high oxygen content compound selected from the group consisting of triacetin, triethyleneglycoldinitrate, dibutyloxylate, dibutyltartrate, dinitroethylenebenzene, dinitrotoluene, and diethylenecyclo-dinitrate as at least a portion of said plasticizing agent.

20. A solid propellant composition consisting essentially of, in parts by weight per 100 parts of a copolymer defined hereinafter: from 500 to 1,000 parts of a solid inorganic oxidizing salt as an oxidizer component; and a binder component comprising 100 parts by weight of a copolymer of (a) a conjugated diene containing from 4 to 8 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 substituent is not more than 15 and wherein R₁ is selected from the group consisting of hydrogen and a methyl radical, and from 10 to 50 parts of a high nitrogen content material selected from the group consisting of melamine, oxamid, RDX (1,3,5-trinitro-1,3,5-triazocyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane), ammonium picrate, ethylenedinitramine, trinitrotoluene, dicyandiamide, urea, and hydrazine nitrate.

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