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2,993,769

SOLID PROPELLANT COMPOSITIONS

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This invention relates to solid propellant compositions. In one aspect this invention relates to solid propellant compositions having improved storage properties. In another aspect this invention relates to a method for preparing solid propellant compositions having improved storage properties.

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 production of such solid propellant compositions, it is desirable that the products have good burning rate and good mechanical properties, such as high elongation and high tensile strength, after extended storage as well as initially. It is also desirable that the propellant compositions be non-brittle and resistant to cracking or fissuring when subjected to temperature cycling.

It is frequently desired to prepare propellant compositions of the above-described types having higher specific impulse and higher density than normal. One method of preparing such propellants is to increase the concentration of the oxidant component to near its stoichiometric ratio with the binder component. However, at high concentrations of oxidant component the amount of the binder component present approaches the amount insufficient to form a continuous matrix in which to disperse the oxidant component. The flow properties of such a composition are such that the material can be extruded by conventional means only with extreme difficulty. Indeed, such propellants having high oxidant component contents are usually compression molded rather than extruded.

While such a method of forming propellants containing high concentrations of oxidant has been successful, two difficulties are sometimes encountered in manufacturing compression molded propellants of this type. One of these difficulties is brittleness, i.e., the inability to withstand shock or be deformed without breaking. A second difficulty sometimes encountered with ammonium nitrate propellants having low concentrations of binder component has been cracking due to thermal cycling, that is, cycling the temperature of the atmosphere surrounding the propellant grain from -75° to 170° F. in storage tests as described hereinafter. Such thermal cycling causes the ammonium nitrate in the propellant to undergo several phase changes. Because of these difficulties, pressed charges employing high concentrations of oxidant, particularly high concentrations of ammonium nitrate, have not been developed to any large degree, primarily due to the inadequacy of presently used binders.

We have now discovered that propellants containing high oxidant concentration and which can be compression molded into non-brittle, thermally stable, grains can be formulated by employing as the binder component a mixture comprising (1) a petroleum pitch prepared by vacuum distillation of a cracked petroleum residue and (2) a rubbery polymer.

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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 improved storage properties. Still another object of this invention is to provide non-brittle, thermally stable, propellant compositions. Still another object of this invention is to provide a method of preparing said improved propellant composition. 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: from 75 to 95 weight percent of a solid inorganic oxidizing salt as an oxidant component; and from 5 to 25 weight percent of a binder component comprised of a mixture of (1) a highly reduced petroleum residue having a softening point within the range of 190 to 250° F., and a penetration within the range of 0 to 5 at 115° F. and (2) a rubbery polymer.

Further, according to the invention there is provided a method for the preparation of a non-brittle, thermally stable, solid propellant composition, which method comprises: dissolving a rubbery polymer in a suitable solvent to form a solution; adding a petroleum pitch prepared by vacuum distillation of a cracked petroleum residue to said solution to form a first dispersion of said pitch in said solution; incorporating a solid inorganic oxidizing salt in said first dispersion to form a second dispersion; and applying heat and vacuum to said second dispersion to remove said solvent therefrom.

The weight ratio of said petroleum pitch to the rubbery polymer in the binder component of the propellant compositions of the invention is usually within the range 50:50 to 90:10, preferably within the range 60:40 to 85:20.

The term "petroleum pitch" as used herein refers to a material prepared by vacuum distillation of a cracked petroleum residue. One method of preparing such a material comprises charging a topped crude oil to a first thermal cracking unit and cracking said topped crude oil at a temperature within the range of about 850 to 1000° F. and a pressure within the range of 50 to 150 p.s.i.g., preferably as near atmospheric pressure as possible. The operating conditions employed in said first cracking unit are, in general, those employed in what is known in the art as a vis-breaking operation, i.e., high velocity of oil through the cracking coil, high heat transfer rates, etc. Usually such an operation is a once-through operation. The effluent from the cracking coil is fractionated to separate a fuel oil or residue which is then charged to a second cracking unit. In said second cracking unit the residue from the first cracking unit is further cracked at a temperature of at least 900° F., and a pressure within the range of 50 to 400 p.s.i.g. The second cracking zone is operated under what are known in the art as severe cracking conditions, i.e., low velocity of oil through the cracking coil and is frequently a recycle operation. In such a severe cracking operation the upper temperature limit is limited only by consideration of such factors as nature of the oil charged, desired properties of products produced, equipment limitations, etc., since the object is to crack the oil as much as possible. The residue from the severe cracking zone is then charged to a vacuum still at a temperature within the range of 600 to 900° F. wherein it is vacuum distilled at a pressure within the range of 0.01 to about 20 millimeters Hg pressure, preferably within the range of 0.01 to about 8 millimeters Hg. The residue from the vacuum still comprises the special petroleum pitch used in the propellant compositions of the invention.

In another method of preparing the special petroleum pitch of the invention the cracked topped crude from the

mild cracking step described above is passed to a vacuum distillation step and the residue from said vacuum distillation is then passed to the above-described severe cracking operation. The residue from the severe cracking operation is then vacuum distilled as described above to produce the petroleum pitch used in the propellant compositions of the invention.

In still another method for preparing the special petroleum pitch used in the propellant compositions of the invention an aromatic diluent oil is incorporated with the oil charged to the severe cracking step. With some oils this is desirable because the presence of the aromatic diluent will permit more severe cracking with less coke formation. Further details regarding the above described methods for the preparation of the petroleum pitch used in the propellant compositions of the invention can be found in Patent No. 2,756,186, issued July 24, 1956 to C. H. Owen et al.

Petroleum pitches within the scope of the invention are characterized by a softening point (ring and ball method) within the range of 190 to 250° F. and a penetration value within the range of 0 to 5 at 115° F. (100 grams for 5 seconds). Said petroleum pitches are further characterized by an asphaltene content of about 70 to 75 weight percent and a maltene content of about 25 to 30 weight percent. Asphaltenes can be defined as that portion of the pitch which is insoluble in or is precipitated by an excess of such light hydrocarbons as normal pentane, cyclopentane, normal hexane, normal heptane, petroleum ether, etc. Maltenes can be defined as those compounds present in said pitch which are completely soluble in said light hydrocarbons during the separation of the asphaltenes. Said petroleum pitches are further characterized by a high aromatics content and essentially no content of naphthenes. Physical properties of a typical petroleum pitch prepared as desired above are:

Softening point (R & B) ° F.	240
Specific gravity at 60° F.	1.1
Penetrations (100 g. 5 sec.):	
At 77° F.	0
At 100° F.	0
At 115° F.	1
At 130° F.	2
At 150° F.	10
Solubilities:	Wt. percent
In carbon disulfide	99.2
In benzene	97.8
In carbon tetrachloride	89.3
Elemental analysis:	
Wt. percent	
C	87.3
H	7.4
N	0.23
S	2.17
Ash	1.28
Water	0.29
	98.67
Other (oxygen, etc.)	1.33

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

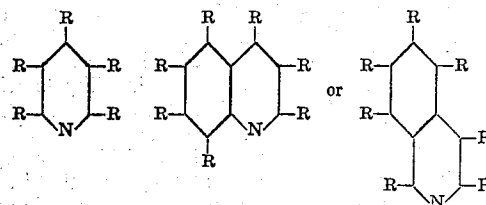
Instead of using a single conjugated diene, a mixture of conjugated dienes can be employed. Thus, a mixture of 1,3-butadiene and isoprene can be employed as the conjugated diene portion of the monomer system.

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



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-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 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 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 hereinafter described and the petroleum pitch and, in addition, there can be present one or more reinforcing agents, plasticizers, wetting agents, and antioxidants. Other ingredients which are employed for sulfur vulcanization include a vulcanization accelerator, a vulcanizing agent, such as sulfur, and an accelerator activator, such as zinc oxide. The finished binder usually contains various compounding ingredients. Thus, it will be understood that herein and in the claims, unless otherwise specified the term "binder" is employed generically and includes various conventional compounding ingredients. The binder content of the propellant composition will usually range from 5 to 25 percent by weight.

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, 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
Petroleum pitch	100-900

In addition other ingredients can be included as follows:

	Parts by weight
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), 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.

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 mixtures of plasticizers rather than a single material.

Oxidizers which are applicable in the solid propellant compositions of this invention are those oxygen-containing solids which readily give up oxygen and include, for example, ammonium, alkali metal, and alkaline earth metal salts of nitric, perchloric, and chloric acids, and mixtures thereof. Ammonium nitrate and ammonium perchlorate are the preferred oxidizers for use in the solid propellants of this invention. Other specific oxidizers include sodium nitrate, potassium perchlorate, lithium chlorate, calcium nitrate, barium perchlorate, and strontium chlorate. Mixtures of oxidizers are also applicable. In the preparation of the solid rocket propellant compositions, the oxidizers are ground to a particle size, preferably within the range between 20 and 200 microns average particle size. The most preferred particle size is from 40-60 microns. The amount of solid oxidizer used is a major amount of the total composition and is in the range of 75 to 95 percent by weight of the total propellant composition. When ammonium

nitrate is used as the oxidant component it is preferred to use a phase stabilizing 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.

Any suitable burning rate catalyst can be used in the propellant compositions of the invention. Burning rate catalysts applicable in the invention include ammonium dichromate and metal ferrocyanides and ferricyanides. 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 ferricyanide (Turnbull's blue) is also applicable. A particularly effective burning rate catalyst is Milori blue which is 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 weight percent, preferably within the range of 0.5 to 2.0 weight percent of the total composition.

The various ingredients in the propellant composition can be mixed on a roll mill or an internal mixer such as a Banbury, or a Baker-Perkins dispersion blade mixer can be employed. 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 addition of oxidant ingredient. The binder ingredients are mixed to form a binder mixture and the oxidizer ingredient is then added to said binder mixture in four equal subsequent additions.

Another method of mixing the ingredients of the propellant composition comprises a solvent mixing technique. In this method the rubbery polymer is dissolved in an excess of a suitable solvent to form a solution. The petroleum pitch is then added to the rubber solvent solution to form a first dispersion of said pitch in said solution since said pitch is usually not completely soluble in said solution. The solid components of the propellant composition such as the oxidant and the burning rate catalyst are then incorporated into said first dispersion to form a second dispersion. After said solid ingredients are thoroughly dispersed, heat and vacuum are applied and the excess solvent is removed.

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 within 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 curing temperature will be limited by the oxidizer employed in some instances but will generally be in the range between 70 and 240° F. Curing can be effected at atmospheric pressure or under superatmospheric pressures. It is usually preferred to cure at about atmospheric pressure. Therefore it is preferred that the curing temperature not be above about 10° F. less than the softening point of the particular petroleum pitch employed. The curing time must be long enough to give the required creep resist-

ance and other mechanical properties in the propellant. The time will generally range from around three hours when the higher curing temperatures are employed to about seven days when curing is effected at lower temperatures.

The following examples will serve to further illustrate the invention.

EXAMPLE I

A series of runs were made in which propellant compositions were formulated and pressed into propellant grains. These runs were carried out according to the following procedure.

A propellant binder composition was made up which contained the following ingredients.

Binder composition

	Parts by weight
Petroleum pitch	280
90/10 copolymer of 1,3-butadiene/2-methyl-5-vinylpyridine	100
Low abrasion furnace black	20
Stabilizer	3

The petroleum pitch in the above formulation had a softening point of 240° F. by the ring and ball method, a penetration value at 115° F. (100 grams for 5 seconds) of 0 and a specific gravity of approximately 1.1. The analysis of this pitch was: carbon—87.3 weight percent, hydrogen—7.4 weight percent, nitrogen—0.23 weight percent, sulfur—2.17 weight percent, ash—1.28 weight percent, and water—0.29 weight percent. The butadiene-2-methyl-5-vinylpyridine copolymer was prepared by emulsion polymerization according to the following recipe. The polymerization was carried out at 41° F.

Polymerization recipe

Ingredient:	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 ethylenediaminetetracetic acid	0.005
Tertiary dodecyl mercaptan (modifier)	(¹)
Ferrous sulfate heptahydrate	0.2
Potassium pyrophosphate	0.253
Para-methane hydroperoxide	0.135
Shortstop - potassium dimethyldithiocarbamate	2 0.15
Stabilizer-phenyl-β-naphthylamine	2 1.75

¹ Fifty-five runs were made using the above polymerization recipe. The latex was masterbatched with 19.5 parts of Philblack A (a trademark of Phillips Petroleum Company for a low abrasion furnace carbon black) per 100 parts of rubber. The black masterbatch was then acid coagulated, washed with water, and dried. The average conversion for these 55 runs was 85 percent in 17.0 hours. The amount of modifier used in each run was in the range of 0.60 to 0.80 part by weight. ² Based on 100 parts by weight of rubber.

One-half part by weight per 100 parts of rubber of additional low abrasion furnace carbon black and 1.25 parts by weight (on the same basis) of a physical mixture containing 65 percent of a complex diarylamine-ketone reaction product and 35 percent of N,N'-diphenyl-p-phenylenediamine were milled into the rubber prepared as described above. This increased the amount of carbon black present to 20 parts per 100 parts of rubber and increased the amount of stabilizer present to 3 parts per 100 parts of rubber.

As shown above in the binder composition, 20 parts by weight of carbon black was present. All of the carbon black present in the propellant was charged as an ingredient of the binder.

The rubber, containing carbon black, was dissolved in methylcyclohexane, after which the pitch was added to the solution. Some of the pitch dissolved, and the result-

ing dispersion of pitch in rubber-pitch-methylcyclohexane solution contained 66.66 percent by weight methylcyclo-

lengths of time. These ballistic data are given below in Table II.

TABLE II
AVERAGE BALLISTIC DATA OBTAINED ON CONTROL GRAINS AND STRANDS

Motor Data					Strand Data				
Test Temp., ° F.	O* Charac- teristic Exhaust Velocity, ft./sec.	Pressure Expo- nent, 600 p.s.i. and 1,000 p.s.i.	Burning rate at 600 p.s.i., in./sec.	Burning rate at 1,000 p.s.i., in./sec.	Burning rate at 600 p.s.i., in./sec.	Pressure Expo- nent at 600 p.s.i.	Burning rate at 1,000 p.s.i., in./sec.	Pressure Expo- nent at 1,000 p.s.i.	Pressure Range (p.s.i.)
74.....	4,399	0.62	0.159	0.222	0.167	0.65	0.245	0.75	300-1,150
BALLISTIC DATA ON GRAINS AND STRANDS AGED ONE MONTH AT 170° F.									
73.....	4,300	0.62	0.164	0.230	0.165	0.65	0.237	0.71	300-1,500
BALLISTIC DATA ON GRAINS AND STRANDS AGED THREE MONTHS AT 170° F.									
75.....	4,127	0.62	0.175	0.245	0.165	0.65	0.224	0.60	300-1,650
BALLISTIC DATA ON GRAINS AND STRANDS AGED SIX MONTHS AT 170° F.									
75.....	4,215	0.62	0.174	0.244	0.165	0.65	0.228	0.64	300-1,740

The propellant composition of these runs was tested for strength and other physical properties. The results of these tests are given below in Table III. The results there reported are averages for the number of tests made.

hexane. The formation of the solution was carried out at 170° F. in a heated Baker Perkins mixer equipped with a vacuum head.

Phase-stabilized ammonium nitrate and ammonium dichromate were then added to the dispersion after which the solvent was removed by evaporation under vacuum. The phase-stabilized ammonium nitrate was prepared by admixing 90 parts of ammonium nitrate and 10 parts of potassium nitrate with some water, heating the mixture to about 140° F., drying, and grinding to approximately 40 micron particle size.

The composition of the final propellant is given below.

Propellant composition

	Parts by Weight	Weight Per- cent
Ammonium nitrate.....	84.6	82.95
Potassium nitrate.....	9.4	9.22
Petroleum pitch.....	4.2	4.11
90/10 BD/MVP copolymer ¹	1.8	1.76
Ammonium dichromate.....	2.0	1.96
Total.....	102.0	100.00

¹ Containing 20 parts/100 parts of rubber of low abrasion furnace black, and 3 parts/100 parts of rubber of stabilizer.

The propellant composition was then pressed into 3" O.D. x 1½" I.D. x 5" long cylindrical, centrally perforated motor grains at room temperature utilizing a pressure of 10,000 p.s.i. and a press time of 10 minutes. The grains were loaded into a small motor and fired at 70° F. The results are given below in Table I.

TABLE I

Burning rate, at 70° F.:	
At 1,000 p.s.i., inch/sec.....	0.26
At 600 p.s.i., inch/sec.....	0.22
Pressure exponent, <i>n</i>	0.44
Characteristic exhaust velocity, ft./sec.....	4500
Density, lbs./cu. inch.....	0.061

Grains of another batch of the above propellant composition were tested for ballistic properties after storage for various lengths of time. Strands approximately ⅛" in diameter and 7" in length were also formed under the above described conditions. Said strands were also tested for ballistic properties after storage for various

TABLE III

Aging Time and Temp. (hr. at ° F.)	No. of Tests	Test Temp., ° F.	Rate of Loading (inches/ min.)	Ulti- mate Stress, p.s.i.	Ulti- mate Elong- ation (per- cent)	Modu- lus of Elas- ticity
Unaged.....	4	70	2	576	2.5	23,930
Do.....	2	170	2	203	2.1	12,870
Do.....	1	-75	2	1,871	-----	51,630
One mo. at 170.....	4	75	2	717	2.16	26,550
24 at 180.....	4	75	2	565	1.8	32,550

Propellant grains of the above-described composition withstood 65 cycles of thermal shocking between -75 and 170° F. without damage. A similar propellant in which the binder was all petroleum pitch, formed microscopic cracks after 15 cycles.

EXAMPLE II

A propellant composition was made up containing the same ingredients as were used in Example I, except that the ratio of petroleum pitch to total of rubber plus carbon black and stabilizer was 90/10 (by weight) instead of 70/30 as in Example I.

In this run, the pitch and rubber were blended together on a roll mill until the mixture was homogeneous, after which the mixture was ground to 20-40 micron size. This finely divided binder was then blended with the oxidant and catalyst in a Twin-shell blender. The dry blended composition was then pressed into grains and strands like those of Example I at room temperature utilizing 10,000 p.s.i. pressure and a 10 minutes press time. The specific propellant composition was as follows:

Propellant composition

Ingredient	Parts by Weight	Weight Percent
Oxidant:		
Ammonium nitrate.....	84.6	82.95
Potassium nitrate.....	9.4	9.22
Binder:		
Refinery pitch.....	5.4	5.29
90/10 BD/MVP copolymer ¹	0.6	0.58
Catalyst: Ammonium dichromate.....	2.0	1.96
Total.....	102.0	100.00

¹ Identical with the copolymer of Example I.

The ballistic data for the above propellant composition are given below in Table IV.

TABLE IV

Burning rate at 70° F.:	
At 1000 p.s.i., inch/second	0.24
At 600 p.s.i., inch/second	0.18
Pressure exponent, <i>n</i>	0.52
Characteristic exhaust velocity, ft./second	4250
Density, lbs./cu. in.	0.061

EXAMPLE III

A propellant composition was made up containing the same ingredients in the same amount and employing the mixing procedure of Example I, except that the oxidizer used was all ammonium nitrate instead of phase stabilized ammonium nitrate. Tensile specimens were molded under three temperature conditions, using a mold pressure of 10,000 p.s.i. and a molding time of 10 minutes. The results of these tests are given below in Table V. Results reported are averages for the number of tests shown.

TABLE V

No. of Tests	Molding Conditions	Ultimate Stress, p.s.i.	Ultimate Elongation, Percent	Modulus of Elasticity (p.s.i.)
3	Propellant and mold at room temperature	510	2.8	18,000
4	Propellant at 180° F., mold at room temperature.	430	2.8	15,000
4	Mold at 220° F., propellant at room temperature.	440	2.3	20,000

EXAMPLE IV

Two propellant compositions A and B were made using the same binder and oxidant as was used in Example I. The mixing was carried out by the solvent technique described in Example I. In these runs, catalysts other than ammonium dichromate were used.

Propellant compositions

Ingredients	Parts by Weight		Weight Percent	
	A	B	A	B
Oxidant:				
NH ₄ NO ₃	84.6	84.6	82.95	82.95
KNO ₃	9.4	9.4	9.22	9.22
Binder:				
Petroleum pitch (like Example I)	4.2	4.2	4.11	4.11
90/10 BD/MVP copolymer of Example I	1.8	1.8	1.76	1.76
Catalyst:				
Copper chromite	2.0	0.0	1.96	0.00
Rouge (Ferric oxide)	0.0	2.0	0.00	1.96
Total	102.0	102.0	100.00	100.00

The above compositions were pressed into strands like those of Example I at 10,000 p.s.i. for 10 minutes at room temperature and tested in a conventional strand burning bomb. The strands were not cured. The data from the strand burning tests are given below in Table VI.

TABLE VI

Propellant Composition	Firing Temperature	Burning Rate at 600 p.s.i. (in./sec.)	Burning Rate at 1,000 p.s.i. (in./sec.)	Pressure Exponent, <i>n</i>	Pressure Range, p.s.i.
A	70	0.127	0.191	0.78	300-1,735
B	70	0.100	0.148	0.77	300-1,675

EXAMPLE V

The propellant composition of the invention was tested against propellant compositions of the prior art which contained conventional petroleum asphalts prepared by vacuum distillation of topped crude oil. Said asphalts are characterized by low aromaticity, the presence of some naphthenic compounds, and an asphaltene content between about 25 and about 50 weight percent. The ingredients of the compositions were mixed together by dry blending, except for propellant H which was mixed together by the solvent technique of Example I. The compositions were pressed into rocket motor grains like those of Example I at 10,000 p.s.i. at room temperature, using a mold time of 10 minutes. The recipes for the compositions were as follows.

Propellant compositions

Ingredients	Propellants							
	E		F		G		H	
	Pts. by Wt.	Wt. Percent	Pts. by Wt.	Wt. Percent	Pts. by Wt.	Wt. Percent	Pts. by Wt.	Wt. Percent
Oxidant:								
NH ₄ NO ₃	84.6	82.95	84.6	82.95	84.6	82.95	84.6	82.95
KNO ₃	9.4	9.22	9.4	9.22	9.4	9.22	9.4	9.22
Binder:								
170° F. softening point petroleum asphalt	6.0	5.87			4.2	4.11		
270° F. softening point petroleum asphalt			6.0	5.87				
240° F. softening point petroleum pitch (identical to Ex. I)							4.2	4.11
90/10 BD/MVP copolymer (identical to Ex. I)					1.8	1.76	1.8	1.76
Catalyst: Ammonium dichromate	2.0	1.96	2.0	1.96	2.0	1.96	2.0	1.96
Total	102.0	100.00	102.0	100.00	102.0	100.00	102.0	100.00

The motor grains of the above compositions were shock cycled between -75 and 170° F. Propellant E failed after 15 cycles, propellant F failed after 5 cycles, propellant G failed after 10 cycles, while propellant H, an example of the propellants of the invention withstood 65 cycles before failing.

EXAMPLE VI

Two propellant formulations were made up according to the following recipes. Both of these propellant formulations were made up by the solvent mixing technique described in Example I.

	Propellant Formulations			
	J		K	
	Parts by Wt.	Wt. Percent	Parts by Wt.	Wt. Percent
Petroleum Pitch (240° F. softening point) (like Ex. I)	4.0	3.92	0.0	-----
Petroleum Asphalt (270° F. softening point)	-----	-----	4.0	3.92
20-Mooney 90/10 Butadiene/2-methyl-5-vinylpyridine copolymer	2.0	1.96	2.0	1.96
Ammonium nitrate (phase stabilized)	94.0	92.16	94.0	92.16
Ammonium dichromate	2.0	1.96	2.0	1.96
Total	102.0	100.00	102.0	100.00

Each of these propellant formulations was pressed into cylinders 1.5" O.D. x 1.5" long using 10,000 p.s.i. pressure. These cylinders were then shock cycled between -75 and 170° F. Propellant formulation K failed at 10 cycles, while propellant formulation J, representing the invention, did not fail until 65 cycles had been completed.

The results given in Examples V and VI above clearly demonstrate the superiority of the propellant compositions of the invention when propellant grains made from said compositions are subjected to thermal cycling tests. Said thermal cycling tests are carried out to simulate conditions which rocket propellant grains may be subjected to in actual use. In other words, said grains in actual use might be stored under either low temperature arctic conditions or high temperature desert conditions. Said test has been devised to include and subject the grains to these extremes of temperature. In carrying out thermal cycling tests the propellant grains are stored at a temperature of -75° F. for a period of 24 hours and then removed from said storage and placed immediately in an oven maintained at 170° F. for a period of 24 hours. At the end of the second 24 hours said grains are immediately returned to the -75° F. conditions for 24 hours and then returned to said 170° F. oven for another 24 hour period. The described cycles are repeated for the desired number of times or until the propellant grains show evidence of failure.

The described thermal cycling test is clearly a severe test. Some composite propellants comprising a solid oxidant dispersed in a binder exhibit a tendency to develop fissures or cracks when subjected to said thermal cycling tests. It is essential that the propellant grains not develop these fissures or cracks because when the grain is fired, as in a rocket motor, the presence of a crack or fissure increases the surface of the burning area and thus changes the operating characteristics of the motor in which the propellant grain is fired. Obviously such changes can not be tolerated where reproducible results must be obtained. Composite propellants containing ammonium nitrate are sometimes more prone to form said fissures and cracks when the propellant grains are subjected to thermal cycling tests because of the phase changes which the ammonium nitrate goes through under changes in temperature. Thus the data in Example V showing that propellant H prepared in accordance with the invention

withstood 65 cycles before failing whereas propellants E, F, and G all failed after 15 cycles or less, clearly demonstrates the outstanding and unexpected superiority of the binder component of the invention. The binder component of propellant H was a mixture of the special petroleum pitch and 90/10 Bd/MVP copolymer, and was clearly superior to the binder components of propellants E, F, and G wherein the binder component was a conventional asphalt or a mixture of said asphalt with said copolymer.

Example VI illustrates the outstanding and unexpected superiority of a binder component of the invention comprising a mixture of the special petroleum pitch and 90/10 Bd/MVP copolymer over a similar binder comprising a mixture of a conventional petroleum asphalt and said copolymer.

The physical tests, i.e., ultimate stress and ultimate elongation, reported in Tables III and V above were determined in accordance with the procedure given in ASTM method of test D638-56T except that in the data reported in Table III the rate of loading or speed at which the tensile bar was pulled was 2" per minute instead of the 0.2" per minute specified by said ASTM test.

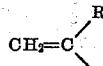
The strand burning test reported in the above examples were determined on strands which were approximately $\frac{3}{16}$ " in diameter and 7" in length and all surfaces thereof except one end were restricted so as to prevent burning except on said one end. In carrying out said tests the strands were 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 5 inches 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, take-off 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 comprising: from 75 to 95 weight percent of a solid inorganic oxidizing salt as an oxidant component; and from 5 to 25 weight percent of a binder component comprised of a mixture of (1) a petroleum pitch, characterized by a high aromatics content and essentially no content of naphthenes, having a softening point within the range of 190 to 250° F. and a penetration within the range of 0 to 5 at 115° F., said pitch having been prepared by vacuum distillation of a cracked petroleum residual oil and (2) a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with styrene, and copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with a

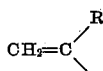


substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine and alkyl substituted quinoline wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15 and wherein R is selected from the group consisting of hydrogen and a methyl radical, said

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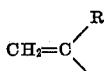
pitch and said polymer being present in a weight ratio of pitch to polymer within the range of 50:50 to 90:10.

2. A non-brittle, thermally stable, solid propellant composition consisting essentially of: from 75 to 95 weight percent of a solid inorganic oxidizing salt as an oxidant component; from 5 to 25 weight percent of a binder component comprised of a mixture of (1) a petroleum pitch, characterized by a high aromatics content and essentially no content of naphthenes, having a softening point within the range of 190 to 250° F. and a penetration within the range of 0 to 5 at 115° F., said pitch having been prepared by vacuum distillation of a cracked petroleum residual oil at a temperature within the range of 600 to 900° F. and a pressure within the range of 0.01 to 20 millimeters of mercury and (2) a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with styrene, and copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with 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, said pitch and said polymer being present in a weight ratio of pitch to polymer within the range of 50:50 to 90:10.

3. A method for the preparation of a non-brittle, thermally stable, solid propellant composition comprising: from 75 to 95 weight percent of a solid inorganic oxidizing salt as an oxidant component; and from 5 to 25 weight percent of a binder component comprised of a mixture of (1) a petroleum pitch, characterized by a high aromatics content and essentially no content of naphthenes, having a softening point within the range of 190 to 250° F. and a penetration within the range of 0 to 5 at 115° F. and (2) a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with styrene, and copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with a

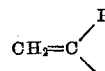


substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine and alkyl substituted quinoline wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15 and wherein R is selected from the group consisting of hydrogen and a methyl radical; which method comprises: dissolving said rubbery polymer in a suitable solvent to form a solution; then adding said petroleum pitch to said solution to form a first dispersion of said pitch in said solution; then incorporating said solid inorganic oxidizing salt in said first dispersion to form a second dispersion; and then applying heat and vacuum to said second dispersion to remove said solvent therefrom said pitch and said polymer being present in a weight ratio of pitch to polymer within the range of 50:50 to 90:10.

4. A composition of matter consisting essentially of a mixture of (1) a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with styrene; and co-

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polymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with a



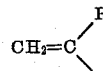
substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine and alkyl substituted quinoline wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15 and wherein R is selected from the group consisting of hydrogen and a methyl radical, and (2) a petroleum pitch, characterized by a high aromatics content and essentially no content of naphthenes, having a softening point within the range of 190 to 250° F., and a penetration within the range of 0 to 115° F., said pitch and said polymer being present in a weight ratio of pitch to polymer within the range of 50:50 to 90:10, said pitch having been prepared by vacuum distillation of a cracked petroleum residual oil.

5. The composition of claim 1 wherein said oxidant component is ammonium nitrate.

6. The composition of claim 1 wherein said oxidant component is phase stabilized ammonium nitrate.

7. The composition of claim 1 wherein said oxidant component is ammonium perchlorate.

8. The composition of claim 1 wherein said rubbery polymer is a copolymer of (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. The composition of claim 8 wherein said copolymer is a copolymer of 1,3-butadiene and 2-methyl-5-vinyl pyridine.

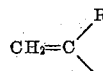
10. The composition of claim 1 wherein said rubbery polymer is a copolymer prepared by copolymerizing 1,3-butadiene with styrene.

11. The method of claim 3 wherein said oxidant component is ammonium nitrate.

12. The method of claim 3 wherein said oxidant component is phase stabilized ammonium nitrate.

13. The method of claim 3 wherein said oxidant component is ammonium perchlorate.

14. The method of claim 3 wherein said rubbery copolymer 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.

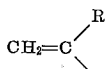
15. The method of claim 14 wherein said copolymer is a copolymer of 1,3-butadiene and 2-methyl-5-vinyl pyridine.

16. The composition of claim 1 wherein said rubbery polymer is a copolymer prepared by copolymerizing 1,3-butadiene with styrene.

17. A non-brittle, thermally stable, solid propellant composition comprising: from 75 to 95 weight percent of a solid inorganic oxidizing salt as an oxidant component; from 5 to 25 weight percent of a binder component comprised of a mixture of (1) a petroleum pitch,

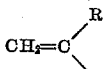
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characterized by a high aromatics content and essentially no content of naphthenes, prepared by vacuum distillation of a cracked petroleum residual oil at a temperature within the range of 600 to 900° F. and a pressure within the range of 0.01 to 20 millimeters of mercury, said pitch being characterized by a softening point within the range of 190 to 250° F., a penetration within the range of 0 to 5 at 115° F., an asphaltene content within the range of about 70 to about 75 weight percent, and a maltene content within the range of about 30 to about 25 weight percent, and (2) a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with styrene, and copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with 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, said pitch and said polymer being present in a weight ratio of pitch to polymer within the range of 50:50 to 90:10.

18. The composition of claim 17 wherein said rubbery polymer 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.

19. A non-brittle, thermally stable, solid propellant composition comprising: from 75 to 95 weight percent of a solid inorganic oxidizing salt as an oxidant component; from 5 to 25 weight percent of a binder component comprised of a mixture of (1) a petroleum pitch, characterized by a high aromatics content and essentially no content of naphthenes, prepared by vacuum distillation of a cracked petroleum residual oil at a temperature within the range of 600 to 900° F. and a pressure within the range of 0.01 to 20 millimeters of mercury and characterized by the following physical properties:

Softening point (R. & B.) ° F.----- About 240
Specific gravity at 60° F.----- About 1.1
Penetrations (100 g., 5 sec.):

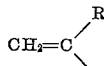
At 77° F.----- About 0
At 100° F.----- About 0
At 115° F.----- About 1
At 130° F.----- About 2
At 150° F.----- About 10

Solubilities: Weight percent
In carbon disulfide----- About 99.2
In benzene----- About 97.8
In carbon tetrachloride----- About 89.3

Analysis: Weight percent
C ----- About 87.3
H ----- About 7.4
N ----- About 0.23
S ----- About 2.17
Ash ----- About 1.28
Water ----- About 0.29

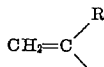
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and (2) a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with styrene, and copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with a



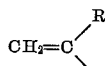
substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine and alkyl substituted quinoline wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 15, and wherein R is selected from the group consisting of hydrogen and a methyl radical.

20. The composition of claim 19 wherein said rubbery polymer 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.

21. A method for the preparation of a non-brittle, thermally stable, solid propellant composition, which method comprises, in combination, the steps of: dissolving a rubbery polymer selected from the group consisting of natural rubber, polybutadiene, polyisobutylene, polyisoprene, copolymers of isobutylene and isoprene, copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with styrene, and copolymers of conjugated dienes containing from 4 to 10 carbon atoms per molecule with 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 in a suitable solvent to form a solution; then adding a petroleum pitch, characterized by a high aromatics content and essentially no content of naphthenes, having a softening point within the range of 190 to 250° F., a penetration within the range of 0 to 5 at 115° F., and having been prepared by vacuum distillation of a cracked petroleum residual oil to said solution to form a first dispersion of said pitch in said solution; then incorporating a solid inorganic oxidizing salt in said first dispersion to form a second dispersion; and then applying heat and vacuum to said second dispersion to remove said solvent therefrom, said pitch and said polymer being present in a weight ratio of pitch to polymer within the range of 50:50 to 90:10.

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