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# PROPELLANT MIXING PROCESS

Charles C. Bice, Bartlesville, Okla., assignor, by mesne assignments, to the United States of America as represented by the Secretary of the Air Force

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This invention relates to a propellant mixing process. In one aspect this invention relates to a process for mixing solid composite type propellants wherein an oxidizer component is dispersed in a rubbery binder component.

Rocket propellants have achieved considerable commercial importance as well as military importance. Jet propulsion motors of the type in which the propellants of this invention are applicable can be employed to aid a heavily loaded plane in take off. Said motors can also be employed as an auxiliary to the conventional power plant when an extra surge of power is required. Said motors can also be employed to propel projectiles and land vehicles. Said propellants can also be used for uses other than propulsion. For example, they can be used as gas generators in starting devices, power units where a fluid is employed as a motive force, and other applications where a comparatively large volume of gas is required in a relatively short period of time.

Solid propellants can be classified with respect to composition as double base type, single base type, and composite type. An example of a double base propellant is "ballistite" which comprises essentially nitroglycerin and nitrocellulose. Examples of single base propellants are nitrocellulose and trinitrotoluene. Composite type propellants are usually composed of a crystalline oxidizer component uniformly dispersed in a fuel matrix which is designated as a binder component. Said composite type propellants may contain other materials to facilitate manufacture or increase ballistic performance, such as a burning rate catalyst. In recent years binder components comprising natural and/or synthetic rubber, together with a reinforcing filler such as carbon black and other rubber compounding and vulcanizing agents, have been widely used in composite type propellants.

Various processes have been proposed for blending the oxidizer component and other "dry" ingredients into the binder component. In one widely used process, frequently referred to as the dry mix method, the oxidizer component and the other dry ingredients are slowly added continuously, or incrementally, to the binder component. Some solid propellant compositions of the composite type are very difficult, if not impossible, to mix by said dry mix method. Difficulties are encountered, particularly when the amount of oxidizer component and other dry ingredients is high, such as above about 83 percent by weight. For example, excessive power may be required to drive the mixing equipment, the mixture may not be sufficiently uniform when it appears to be mixed, or the mixture may be unsuitable for either extrusion or molding into propellant grains.

In another mixing process frequently referred to as the solvent mix technique, the binder component is dispersed or dissolved in a suitable fluid which is a solvent for the rubber. The oxidizer component and other dry ingredients can be readily mixed with the thus fluidized binder and the solvent is subsequently removed. This solvent mix technique assures a good mixture, i.e., uniform dispersion with low power requirements for the mixing. However, due to the relatively large amounts of solvent required, solvent removal and recovery costs are appreciable and in many instances almost prohibitive. In the use of solid propellants as gas generators, and particularly for the propulsion of rockets and other missiles, maximum performance per unit weight of propellant is highly important. However, due to the above-described difficulties with many compositions, good performance is often sacrificed in order to obtain a composition which can be readily processed.



I have found that the above-described difficulties can be eliminated or at least mitigated, and such difficultly processable propellant compositions can be mixed to contain high percentages of oxidizer component and other solid "dry" ingredients by first mixing a portion of said oxidizer component and/or said other solid ingredients with the binder component, then adding a relatively small amount of a solvent for said binder component, and then incorporating the remainder of said solid ingredients.

An object of this invention is to provide an improved propellant composition. Another object of this invention is to provide a process for mixing composite type propellants. Another object of this invention is to provide a process for mixing composite type propellants which process is particularly suitable for propellants having high oxidizer contents or solids loadings. Still another object of this invention is to provide a process for mixing propellants of a composite type wherein a portion of the oxidizer component and/or other solid ingredients is admixed with the binder component to obtain a powdery mass, a relatively small amount of a solvent for the binder is then added to said powdery mass, the remainder of said solid ingredients are then incorporated in said binder, and said solvent is then removed. 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 method for preparing a solid composite type propellant wherein finely divided solid ingredients comprising an oxidizer component are uniformly dispersed in a binder component comprising a rubbery polymer, which method comprises the steps of: mixing successive increments of said solid ingredients into said binder component until a powdery mass is obtained; incorporating a low boiling organic solvent into said powdery mass with sufficient mixing to form a uniform intermediate dispersion; mixing at least one additional increment of said solid ingredients into said intermediate dispersion with sufficient mixing to obtain a final uniform dispersion of said solid ingredients in said binder component; and removing said solvent from said final dispersion.

In the practice of the invention the oxidizer, or oxidizer component together with the other solid "dry" ingredients, is mixed with the binder component gradually or in small increments until the amount of said solid components which have been added is sufficient to obtain a powdery mass. The amount of said solid ingredients necessary to obtain a powdery mass depends upon the type of rubbery polymer and its Mooney value, the amount and kind of rubber compounding ingredients which have been incorporated in said rubbery polymer, and the particle size of said oxidizer component and the other dry solid ingredients. Generally, this amount falls in the range of 78 to 92 weight percent and more commonly within the range of 83 to 88 weight percent of the oxidizer content in the propellant mixture. The exact amount necessary to obtain the powdery mass can be readily ascertained by routine tests for any given propellant composition. As the oxidizer component and/or other solid ingredients is added with continual mixing, the mass in the mixing apparatus becomes more viscous and more power is required to continue mixing. A point is reached where, upon the addition of more oxidizer, a powdery condition is obtained, i.e., the mass in the mixer is transformed from a rubbery mass into a powdery mass. This powdery condition is reflected by a rather

sudden decrease in the power required to operate the mixing equipment. The attainment of this powdery condition is an important aspect of the invention since it permits rapid and uniform wetting of the mass with the solvent. With efficient and properly sized commercial mixers, the mixing time to attain said powdery condition usually falls in the range of about 5 to about 30 minutes.

Upon attaining said powdery condition, the solvent is introduced in any convenient manner so as to uniformly wet the powder. The amount of solvent which is used is usually in the range of 10 to 70 parts by weight per 100 parts by weight of binder component. A more preferred range is about 14 to about 45 parts by weight of solvent for each 100 parts by weight of binder component. Mixing is continued during and after the addition of the solvent to insure uniform distribution of the solvent in the powdery mass. Sufficient mixing is employed to obtain a uniform intermediate dispersion or blend. Usually the time required to add the solvent and to obtain said uniform intermediate dispersion is only of the order of 1 to 5 minutes. It is to be noted that the amount of solvent employed is not sufficient to obtain a solution of the binder component. Said solvent is employed in an amount sufficient to only soften the binder component and upon mixing or milling of the softened binder component the above-mentioned uniform intermediate dispersion of the solid ingredients in the rubbery polymer results. Sometimes, depending upon the amount of solvent used, the powdery mass tends to agglomerate into individual balls or agglomerates which tend to increase in size upon continued mixing. However, said individual balls or agglomerates are uniform dispersions of the solid ingredients in the rubbery polymer and it is not necessary to continue mixing at this stage until all of the individual agglomerated particles have been consolidated into one mass.

After said uniform intermediate dispersion is obtained, the remainder of the oxidizer component and/or other solid ingredients are added with sufficient mixing to obtain a uniform final dispersion of said solid ingredients in the rubbery polymer. Since the invention finds its greatest application in the preparation of solid composite type propellants having high oxidizer contents, the amount of oxidizer added as the last increment is usually sufficient to increase the total oxidizer content of the propellant composition to a value within the range of about 90 to 96 weight percent of the total composition. As indicated above, the oxidizer component can be divided into any suitable number of increments and added incrementally, or it can be added slowly in a continuous manner. If desired the other solid "dry" ingredients employed in the propellant composition can be blended with the oxidizer component and the blend divided into increments or added slowly in a continuous manner. Or, if desired, said other solid dry ingredients can be incorporated or blended with the last increment of oxidizer component.

After all of the oxidizer component and said other dry ingredients have been incorporated into the rubbery polymer with the aid of the solvent as described above, the solvent is then removed. Solvent removal can be effected conveniently by continued mixing in the mixing equipment under reduced pressure, preferably at pressures below 20 millimeters of mercury whereby said solvent is distilled from the propellant mixture. Because of the relatively small amount of solvent present, essentially complete removal of the solvent can be effected within an hour or two, even at temperatures as low as 20 to 25° C. If desired, the mixture can be heated to increase the rate of solvent removal. Quaternizing agents or other curing agents can be added to the propellant mixture before or after the removal of the solvent. If said quaternizing agents are added prior to removal of the solvent, the temperature to which the composition is heated in order to effect solvent removal should be sufficiently low so as to avoid rapid curing of the rubbery polymer. Generally temperatures up to about 60° C. can be employed without danger.

After the solvent has been removed the propellant composition can be formed into propellant grains by extrusion or by compression molding, using conventional techniques known to those skilled in the art.

Any organic liquid having a boiling point at atmospheric pressure below about 120° C., and which is capable of swelling or dissolving the rubbery polymer of the binder component, can be used as the solvent in the practice of the invention. Solvents having a boiling point as low as 20° C. or lower can be used if means are provided to prevent escape of solvent vapors such as carrying out the solvent addition and mixing under pressure. The preferred solvents have a boiling point of about 40 to about 60° C. for convenience in handling. Suitable solvents for use in the practice of the invention include the various hydrocarbon liquids such as hexane, heptane, octane, nonane, cycloheptane, cyclohexane, benzene, toluene, xylene, methylcyclohexane, various naphthas, kerosenes, and the like which have been stripped of high boiling components. Other suitable solvents include the chlorinated hydrocarbons such as carbon tetrachloride, 1,2-dichloroethylene, 1,2-dichloroethane, and the like.

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.

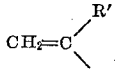
Said preferred class of rubbery polymers prepared by copolymerizing a conjugated diene with a heterocyclic nitrogen base, as well as the other rubbery polymers, can vary in consistency from very soft rubbers, i.e., materials which are soft at room temperature but will show retraction when relaxed, to those having a Mooney value (ML–4 at 212° F.) up to 100. The rubbery polymers most frequently preferred in the practice of the invention have Mooney values in the range between 10 and 60. They may be prepared by any polymerization methods known to the art, e.g., mass or emulsion polymerization. One convenient method for preparing said preferred copolymers is by emulsion polymerization at temperatures in the range between 0 and 140° F. Recipes such as the iron pyrophosphate-hydroperoxide, either sugar-free or containing sugar, the sulfoxylate, and the persulfate recipes are among those which are applicable. It is advantageous to polymerize to high conversion as the unreacted vinylpyridine monomer is difficult to remove by stripping.

The conjugated dienes employed are those containing from 4 to 10 carbon atoms per molecule and include 1,3-butadiene, isoprene, 2-methyl-1,3-butadiene, and the like. Various alkoxy, such as methoxy and ethoxy and cyano derivatives of these conjugated dienes, are also applicable. Thus, other dienes, such as phenylbutadiene, 2,3-dimethyl-1,3-hexadiene, 2-methoxy-3-ethylbutadiene, 2-ethoxy-3-ethyl-1,3-hexadiene, 2-cyano-1,3-butadiene, are also applicable.

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

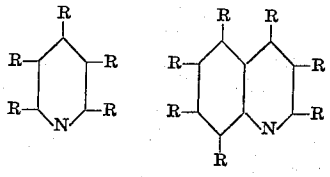
The polymerizable heterocyclic nitrogen bases which

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

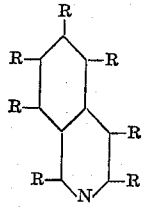


substituent wherein R' is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl (isopropenyl) group. Of these, the compounds of the pyridine series are of the greatest interest commercially at present. Various substituted derivatives are also applicable but the total number of carbon atoms in the groups attached to the carbon atoms of the heterocyclic nucleus should not be greater than 15 because the polymerization rate decreases somewhat with increasing size of the alkyl group. Compounds where the alkyl substituents are methyl and/or ethyl are available commercially.

These heterocyclic nitrogen bases have the formula



or



where R is selected from the group consisting of hydrogen, alkyl, vinyl, alpha-methylvinyl, alkoxy, halo, hydroxy, cyano, aryloxy, aryl, and combinations of these groups such as haloalkyl, alkylaryl, hydroxyaryl, and the like; one and only one of said groups being selected from the group consisting of vinyl and alpha-methylvinyl; and the total number of carbon atoms in the nuclear substituted groups being not greater than 15. Examples of such compounds are 2-vinylpyridine; 2-vinyl-5-ethylpyridine; 2-methyl-5-vinylpyridine; 4-vinylpyridine; 2,3,4-trimethyl-5-vinylpyridine; 3,4,5,6 - tetramethyl-2-vinylpyridine; 3-ethyl-5-vinylpyridine; 2,6-diethyl-4-vinylpyridine; 2-isopropyl-4-nonyl-5-vinylpyridine; 2-methyl-5-undecyl-3-vinylpyridine; 2,4-dimethyl-5,6-dipentyl-3-vinylpyridine; 2-decyl-5-(alpha-methylvinyl) pyridine; 2-vinyl-3-methyl-5 - ethylpyridine; 2-methoxy-4-chloro-6-vinylpyridine; 3-vinyl-5-ethoxypyridine; 2-vinyl-4,5-dichloropyridine– 2-(alpha-methylvinyl)-4-hydroxy-6-cyanopyridine; 2-vinyl-4 - phenoxy-5-methylpyridine; 2 - cyano-5-(alpha-methylvinyl) pyridine; 3-vinyl-5-phenylpyridine; 2-(para-methylphenyl)-3-vinyl-4-methylpyridine; 3-vinyl - 5 - (hydroxyphenyl)-pyridine; 2-vinylquinoline; 2-vinyl-4-ethylquinoline; 3-vinyl-6,7-di-n-propylquinoline; 2-methyl-4-nonyl-6-vinylpyridine; 4 - (alpha-methylvinyl)-8-dodecylquinoline; 3-vinylisoquinoline; 1,6-dimethyl-3-vinylisoquinoline; 2-vinyl-4-benzylquinoline; 3-vinyl-5-chloroethylquinoline-3-vinyl-5,6-dichloroisoquinoline; 2 - vinyl-6-ethoxy-7-methylquinoline; 3-vinyl-6-hydroxymethylisoquinoline; and the like.

Another 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 GH–S rubbers. Said GR–S rubbers can be prepared by any or the well known methods employing well known recipes. Any of the well known GR–S rubbers containing from 1 to 2 and up to about 25 parts of styrene



can be used in the practice of the invention. The GR–S rubber designated as 1505 is one preferred copolymer for use in the practice of the invention. GR–S 1505 can be prepared by copolymerizing 1,3-butadiene with styrene at 41° F. using a sugar free, iron activated, rosin-acid emulsified system. A charge weight ratio of butadiene to styrene is 90/10 and the polymerization is allowed to go to approximately 52 percent completion. The copolymer is then salt acid coagulated and usually has a mean raw Mooney value (ML–4) of about 40. Said copolymers usually have a bound styrene content of about 8 weight percent. Further details regarding the preparation of GR–S rubbers can be found in Industrial and Engineering Chemistry, 40, pages 769–777 (1948) and United States Patents 2,583,277; 2,595,892; 2,609,362; 2,614,100; 2,647,109; and 2,665,269.

The binder contains rubbery polymers of the type hereinbefore described and, in addition, there can be present one or more reinforcing agents, plasticizers, wetting agents, and antioxidants. Other ingredients which are employed for sulfur vulcanization include a vulcanization accelerator, a vulcanizing agent, such as sulfur, and an accelerator activator, such as zinc oxide. The finished binder usually contains various compounding ingredients. Thus, it will be understood that herein and in the claims, unless otherwise specified, the term "binder" is employed generically and includes various conventional compounding ingredients. The binder content of the propellant composition will usually range from 4 to 25 percent by weight.

The rubbery copolymer comprising a conjugated diene and a polymerizable heterocylic 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. Thus, the binder component can also contain a quaternizing agent. Suitable quaternizing agents include, among others, the following: alkyl halides such as methyl iodide, and methyl bromide; alkylene halides such as methylene iodide, and ethylene bromide; substituted alkanes such as chloroform, bromoform, and alkyl sulfates such as methyl sulfate; and various substituted aromatic compounds such as benzoyl chloride, methyl benzene sulfonate, benzo-trichloride, benzyl chloride, benzal chloride, paraxylene-hexachloride, and the like. The quaternizing temperature is usually in the range from 0 to 250° F., although temperatures outside this range can be used.

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

| | Parts by weight |
|---|---|
| Rubbery polymer | 100 |
| Reinforcing agent | 0–50 |
| Plasticizer | 0–100 |
| Wetting agent | 0–10 |
| Antioxidant | 0–3 |
| Vulcanization accelerator | 0–5 |
| Sulfur | 0–2 |
| Quaternizing agent | 0–25 |
| Metal oxide | 0–5 |

Reinforcing agents which can be employed include carbon black, wood flour, lignin, and various reinforcing resins such as styrene-divinylbenzene, methyl acrylate-divinylbenzene, acrylic acid-styrene-divinylbenzene, and methyl acrylate-acrylic acid-divinylbenzene resins.

In general, any rubber plasticizer can be employed in the binder compositions. Materials such as Pentaryl A (amylbiphenyl), 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 dioctylphthalate are suitable plasticizers. Materials which provide a rubber having good low temperature properties are preferred. It is also frequently preferred that the plasticizers be oxygen-containing materials.

One presently preferred plasticizer is a liquid polybutadiene prepared by mass polymerization in the presence of finely divided sodium as the catalyst according to the method of Crouch 2,631,175. Broadly, such plasticizers which can be used in accordance with this invention comprise liquid polymers prepared from conjugated diolefin hydrocarbons such as 1,3-butadiene and isoprene, the liquid polymers having a viscosity of 100 to 5000 Saybolt Furol Seconds at 100° F. Polymers having a viscosity from about 1000 to about 2500 Saybolt Furol Seconds are presently preferred. These liquid polymers can be prepared by emulsion polymerization using large amounts of modifiers in accordance with the teaching of Frolich et al. 2,500,983 although, they are preferably prepared by the method set forth in Crouch 2,631,175. The latter method comprises mass polymerization in the presence of finely divided alkali metal and/or alkali metal hydride such as sodium, potassium, lithium, sodium hydride, potassium hydride and lithium hydride. Polymers thus prepared contain no modifiers or viscosity controlling agent and they are also free of materials which would act as inhibitors such as antioxidants and shortstops. Finely divided catalyst is used, preferably having a particle size below 200 microns, and generally below 100 microns in the range of 40 to 80 microns. The amount of catalyst employed usually does not exceed 2 parts by weight of the total monomer charged, preferably in the range of 0.5 to 1.5 parts by weight per 100 parts monomer. A more complete description of the process is set forth in the Crouch patent identified above.

Another presently preferred plasticizer for use in the propellant compositions of the invention is Philrich 5, a rubber extender and process oil available commercially from Phillips Petroleum Company. Said Philrich 5 is a highly aromatic heavy petroleum residual oil. Typical tests on said Philrich 5 are:

| | |
|---|---|
| Gravity, ° API | 11.6 |
| Viscosity, SUV @ 210° F. | 175 |
| Aniline point, ° F. | 110 |
| Rostler Analysis, wt. percent (IEC 41, 598, 1949): | |
| Asphaltenes | 0.0 |
| Nitrogen bases | 11.0 |
| First acidaffins | 19.0 |
| Second acidaffins | 61.0 |
| Paraffins | 9.0 |

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.

Frequently in the preparation of the binder component the rubbery polymer is masterbatched with the reinforcing filler, mixed with the anti-oxidant, and dried. The resulting masterbatch of polymer, filler, and anti-oxidant is stored and subsequently blended as needed with other ingredients to form the binder component.

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 96 percent by weight of the total propellant composition.

When ammonium nitrate is used as the oxidant component, a phase stabilized ammonium nitrate is frequently used. 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, heating the mixture to about 140° F., dry, and then grind to the desired patricle size.

It is also within the scope of the invention to employ solid organic oxidizing compounds as a portion of the oxidizer component. Examples of said organic oxidizing compounds include, among others, the following: cyclotrimethylene trinitramine, pentaerythritol tetranitrate, cyanoguanidine, nitroguanidine, and guanidine nitrate. Said organic oxidizing compound can be used in an amount ranging from 0 to 10 parts for each 100 parts of solid inorganic oxidizing compound, or, stated another way from about 0 to about 10 weight percent of the total oxidizer content. The organic oxidizing compound replaces a like amount of the inorganic oxidizing compound. Thus, the total amount of solid oxidizing compound in the propellant composition remains within the range of 75 to 96 weight percent of the total propellant composition.

In some instances it is desirable to employ a burning rate catalyst in the propellant compositions of the invention. 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 of the total composition.

It is also within the scope of the invention to include in the propellant composition high energy fuels or propellant additives to increase the specific impulse of the propellant. Examples of said high energy fuels include, among others, finely divided boron, and finely divided metals such as aluminum, magnesium, iron, and alloys of

said metals. Said high energy fuels or additives are usually used in amounts ranging from 0 to 10 weight percent of the total propellant composition.

The following examples will serve to further illustrate the invention.

## EXAMPLE I

A rubbery copolymer was prepared by emulsion polymerization of 1,3-butadiene and 2-methyl-5-vinylpyridine at 41° F. The polymerization recipe was as follows:

*Recipe*

| | Parts by weight |
|---|---|
| 1,3-butadiene | 90 |
| 2-methyl-5-vinylpyridine | 10 |
| Water | 200 |
| Potassium soap | 6 |
| Potassium chloride | 0.1 |
| Sodium salt of condensed alkylaryl sulfonic acid | 0.3 |
| Tetrasodium salt of ethylenediaminetetraacetic acid | 0.005 |
| Tertiary dodecyl mercaptan (modifier) | 0.6–0.8 |
| Ferrous sulfate heptahydrate | 0.2 |
| Potassium pyrophosphate | 0.253 |
| Para-menthane hydroperoxide | 0.135 |

A total of 55 runs were made using the above recipe. The average conversion for these runs was 85 percent in 17.0 hours. The polymerization was shortstopped with 0.15 parts by weight per 100 parts by weight of rubber of potassium dimethyl dithiocarbamate, and 1.75 parts by weight per 100 parts by weight of rubber of phenyl-beta-naphthylamine was added as a stabilizer. The latex was masterbatched with 19.5 parts by weight of a low abrasion furnace carbon black per 100 parts by weight of rubber. The black masterbatch was then coagulated with acid, the crumb was washed with water, and then dried.

The carbon black content of the above-described copolymer product was increased to 22 parts by weight per 100 parts by weight of rubber by milling an additional 2.5 parts of said carbon black into said copolymer.

The thus prepared copolymer masterbatch was placed in a Baker-Perkins mixer and given a preliminary milling. Three parts of Flexamine per 100 parts of copolymer and 20 parts of Butarez 25 per 100 parts of copolymer were then milled into said copolymer masterbatch.

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

| | Parts by Wt. | Weight Percent |
|---|---|---|
| Binder Component | | 13 |
| 90/10 Bd/MVP copolymer | 100 | |
| Carbon black | 22 | |
| Flexamine [1] | 3 | |
| Butarex 25 [2] | 20 | |
| p-Xylene hexachloride | 2.4 | |
| Oxidizer Component | | 87 |
| Ammonium perchlorate | 987 | |
| Ammonium nitrate | 330 | |
| Total | | 100 |

[1] Physical mixture containing 65 percent of a complex diarylamine-ketone reaction product and 35 percent of N,N′-diphenyl-p-phenylenediamine.

[2] Liquid polymer prepared by mass polymerization of 1,3-butadiene using finely divided sodium as catalyst The viscosity at 100° F. is about 2500 centipoises.

The oxidizer was a blend prepared by mixing 330 grams of ammonium nitrate and 987 grams of ammonium perchlorate, each having a weight average particle size, as estimated from screen analysis, of about 40 microns. The oxidizer was divided into six approximately equal portions.

Said rubber masterbatch was placed in a Baker-Perkins mill, and five portions of the oxidizer were added separately over a 15 to 20 minute period. Each portion was mixed to achieve uniform dispersion before addition of the next portion. During addition of the fifth portion the mixture became powdery. This powder mass represented a blend of 15 percent by weight of binder and 85 percent by weight of oxidizer.

Before addition of the sixth and last increment of oxidizer 100 ml. of methylcyclohexane was added to the powdery mass with mixing for a period of 1 to 2 minutes whereupon the mixture was converted to a slightly tacky mass. The last increment of oxidizer was than added and mixed for about 3 minutes so as to obtain a uniform blend. The p-xylene hexachloride was then uniformly incorporated into said blend. Mixing was then continued for about 10 minutes while maintaining the pressure below about one millimeter of mercury pressure within the mixer. The methylcyclohexane was thus removed by distillation. The resulting product had no odor and could be crumbled by pressing between the fingers. When rubbed between the fingers the product felt slightly tacky. The product was moldable. Tubular grains having an O.D. of 3 inches and an I.D. of 1.5 inches and a length of 4 inches were formed in a press. Pressure on the order of 10,000 p.s.i.g. was applied to the propellant composition by means of a piston while forming the propellant grain. The grain was readily removed from the mold, had smooth surfaces and was a uniform blend.

## EXAMPLE II

Another test was made as described above except that 50 cc. of methylcyclohexane was employed. The results were substantially the same, and propellant compositions suitable for use in missiles were obtained.

The above examples illustrate the preparation of compression molded propellant grains from propellant mixes prepared in accordance with the invention. Other tests have shown that high oxidizer content propellant mixes prepared according to the invention can be extruded without the necessity of incorporating extrusion aids.

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.

I claim:

1. A method for preparing a solid composite type propellant wherein finely divided solid ingredients comprising an oxidizer component selected from the group consisting of solid inorganic oxidizing salts, mixtures of said inorganic salts, and mixtures of a solid inorganic oxidizing salt with a solid organic oxidizing compound selected from the group consisting of cyclotrimethylene trinitramine, pentaerythritol tetranitrate, cyanoguanidine, nitroguanidine, and guanidine nitrate wherein the mixture contains up to 10 parts by weight of said organic compound per 100 parts by weight of said inorganic salt, are uniformly dispersed in a binder component comprising a rubbery polymer selected from the group consisting of natural rubber, synthetic rubber polymers, and mixtures thereof, which method comprises, in combination, the steps of: mechanically mixing said solid ingredients into said binder component until a powdery mass is obtained; then incorporating a low boiling organic solvent selected from the group consisting of hexane, heptane, octane, nonane, cycloheptane, cyclohexane, benzene, toluene, xylene, methylcyclohexane, naphtha fractions, kerosene fractions, carbon tetrachloride 1,2-dichloroethylene, and 1,2-dichloroethane, in an amount sufficient to soften said binder component, into said powdery mass with sufficient mechanical mixing to form a uniform intermediate dispersion of said solid ingredients in said binder component; then mechanically mixing at least one additional increment of said solid ingredients into said intermediate dispersion with sufficient mixing to attain a final uniform dispersion of said solid ingredients in said binder component; and then evaporating said solvent from said final dispersion.

2. In the method of preparing a solid composite type propellant wherein solid ingredients comprising a solid oxidizer component selected from the group consisting of

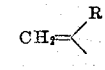
solid inorganic oxidizing salts, mixtures of said inorganic salts, and mixtures of a solid inorganic oxidizing salt with a solid organic oxidizing compound selected from the group consisting of cyclotrimethylene trinitramine, pentaerythritol tetranitrate, cyanoguanidine, nitroguanidine, and guanidine nitrate wherein the mixture contains up to 10 parts by weight of said organic compound per 100 parts by weight of said inorganic salt, are uniformly dispersed in a binder component comprising a rubbery polymer selected from the group consisting of natural rubber, synthetic rubber polymers, and mixtures thereof, the improvement which comprises, in combination, the steps of: mechanically mixing a sufficient quantity of said solid ingredients into said binder component to obtain a powdery mass; then incorporating a low boiling organic solvent selected from the group consisting of hexane, heptane, octane, nonane, cycloheptane, cyclohexane, benzene, toluene, xylene, methylcyclohexane, naphtha fractions, kerosene fractions, carbon tetrachloride, 1,2-dichloroethylene, and 1,2-dichloroethane, in an amount sufficient to soften said binder component, into said powdery mass with sufficient mechanical mixing to form an intermediate uniform dispersion of said solid ingredients in said binder component; then uniformly dispersing with mechanical mixing an additional increment of said solid ingredients into said intermediate dispersion to form a final uniform dispersion of said solid ingredients in said binder component; and then evaporating said solvent from said final dispersion.

3. A method for preparing a solid composite type propellant comprising from 75 to 96 weight percent of an oxidizer component selected from the group consisting of solid inorganic oxidizing salts, mixtures of said inorganic salts, and mixtures of a solid inorganic oxidizing salt with a solid organic oxidizing compound selected from the group consisting of cyclotrimethylene trinitramine, pentaerythritol tetranitrate, cyanoguanidine, nitroguanidine, and guanidine nitrate wherein the mixture contains up to 10 parts by weight of said organic compound per 100 parts by weight of said inorganic salt, and from 25 to 4 weight percent of a binder component comprising a rubbery polymer having a Mooney value (ML–4 at 212° F.) in the range of 10 to 100 and being selected from the group consisting of natural rubber, synthetic rubber polymers, and mixtures thereof, which method comprises, in combination, the steps of: mechanically mixing successive increments of said oxidizer component into said binder component until a powdery mass is obtained; then incorporating from 10 to 70 parts by weight per 100 parts by weight of said binder component of an organic solvent having a boiling point below about 120° C. and selected from the group consisting of hexane, heptane, octane, nonane, cycloheptane, cyclohexane, benzene, toluene, xylene, methylcyclohexane, naphtha fractions, kerosene fractions, carbon tetrachloride, 1,2-dichloroethylene, and 1,2-dichloroethane, into said powdery mass with sufficient mechanical mixing to form a uniform intermediate dispersion of said oxidizer component in said binder component; then mechanically mixing at least one additional increment of said oxidizer component into said intermediate dispersion with sufficient mixing to obtain a final uniform dispersion of said oxidizer component in said binder component; and then evaporating said solvent from said final dispersion.

4. A method for mixing a composite type propellant, which method comprises, in combination, the steps of: mechanically mixing a portion of the oxidizer component with the binder component to obtain a powdery mass, said oxidizer component being selected from the group consisting of solid inorganic oxidizing salts, mixtures of said inorganic salts, and mixtures of a solid inorganic oxidizing salt with a solid organic oxidizing compound selected from the group consisting of cyclotrimethylene trinitramine, pentaerythritol tetranitrate, cyanoguanidine, nitroguanidine, and guanidine nitrate wherein the mixture contains up to 10 parts by weight of said organic compound per 100 parts by weight of said inorganic salt, and said binder component being selected from the group consisting of natural rubber, synthetic rubber polymers, and mixtures thereof; then a low boiling organic solvent selected from the group consisting of hexane, heptane, octane, nonane, cycloheptane, cyclohexane, benzene, toluene, xylene, methylcyclohexane, naphtha fractions, kerosene fractions, carbon tetrachloride, 1,2-dichloroethylene, and 1,2-dichloroethane, into said powdery mass with mechanical mixing in an amount sufficient to only partially dissolve said binder component; then mechanically mixing an additional increment of said oxidizer component into said solvent treated powdery mass; and then evaporating said solvent from the final mixture.

5. A method according to claim 1 wherein said oxidizer component is a mixture of at least one solid inorganic oxidizing salt with at least one solid organic oxidizing compound selected from the group consisting of cyclotrimethylene trinitramine, pentaerythritol tetranitrate, cyanoguanidine, nitroguanidine, and guanidine nitrate, said organic oxidizing compound being present in an amount up to about 10 parts by weight per 100 parts by weight of said inorganic oxidizing salt.

6. A method according to claim 1 wherein said oxidizer component is a mixture of ammonium nitrate and ammonium perchlorate, and 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.

7. A method according to claim 6 wherein said copolymer is a copolymer of 1,3-butadiene with 2-methyl-5-vinylpyridine.

8. A method according to claim 1 wherein said rubbery polymer is a copolymer prepared by copolymerizing 1,3-butadiene with styrene.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,622,277 | Bonell et al. | Dec. 23, 1952 |
| 2,857,258 | Thomas | Oct. 21, 1958 |
| 2,877,504 | Fox | Mar. 17, 1959 |
| 2,962,368 | Guth | Nov. 29, 1960 |

OTHER REFERENCES

Chem. and Eng. News, Oct. 7, 1957, pp. 62, 63.

Baker: Missiles and Rockets, vol. 4, No. 6, Aug. 11, 1958, pp. 45–47.

Kit et al.: "Rocket Propellant Handbook," The MacMillan Co., New York (1960), p. 201.