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3,032,449

COATED SOLID ROCKET PROPELLANTS WITH IMPROVED IGNITION CHARACTERISTICS

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12 Claims. (Cl. 149—7)

This invention relates to the operation of solid propellant rockets. In one of its more specific aspects it relates to a method and means for improving the burning rate of solid rocket propellants. In another of its specific aspects it relates to a method and means for improving ignition of solid rocket propellants at atmospheric pressure.

With rockets utilizing a solid propellant, all of the propellant to be burned is contained within the combustion chamber, therefore, such units are most extensively used for jet-assist-take-off units, rocket bombs and projectiles.

The solid propellant charges utilized are generally classified with reference to their burning as restricted and unrestricted burning type charges. The restricted type is the one which provides for controlled burning, and most propellants have provision for some form of restricted burning. While this invention is applicable to any solid propellant rocket, it is particularly applicable to rockets using a charge of the restricted type.

Solid propellants may be classified with respect to composition as double base type, single base type, and composite type of propellant. An example of a double base propellant is "ballistite" which comprises essentially nitroglycerine and nitrocellulose. Examples of single base propellants are nitrocellulose and trinitrotoluene. Composite type propellants are generally composed of an oxidizer, and a binder or fuel. They may contain other materials to improve fabrication or increase ballistic performance such as a burning rate catalyst. Compounds which can be used as oxidizers include ammonium nitrate and perchlorates such as ammonium perchlorate and potassium perchlorate.

One outstanding disadvantage of many solid propellants is poor ignitability at atmospheric pressure. In composite propellants the difficulty of ignition depends on the oxidizer and to some extent on the binder. Composite propellants containing ammonium nitrate as the oxidizer are notably difficult to ignite. Because of the lower cost and greater potential availability of ammonium nitrate over other oxidizers, this invention becomes especially applicable where this compound is used.

There has recently been developed an improved composite type solid rocket propellant comprising an oxidant, such as ammonium nitrate and a polymeric quaternary ammonium compound. This propellant is produced by mixing a solid oxidant, a liquid copolymer of a conjugated diolefin with a vinyl heterocyclic nitrogen base of the pyridine and quinoline series and a quaternizing agent, placing the mixture which has the consistency of a stiff paste in a mold under pressure, and extruding it in the form of pellets which are cured under controlled conditions. Propellant grains can also be cured in molds under pressure and at quaternizing temperatures of 0 to 175° C. As a result of reaction between the liquid copolymer and the quaternizing agent, the pasty mixture sets to a hard, resilient propellant that is resistant to shock even at low temperatures. Quaternizing agents which can be used include, for example, methyl iodide, benzotrichloride, benzylchloride, diethylbromomalonate and ethyl alpha-chloroacetoacetate. These improved composite propellants and the method of producing them are more fully described in copending application Serial No. 284,447,

filed April 25, 1952 by W. B. Reynolds and J. E. Pritchard entitled "Solid Rocket Propellant Compositions."

There is also described in the above-identified copending application a composite type solid rocket propellant comprising an oxidant such as ammonium nitrate and a vulcanized copolymer of a conjugated diene such as butadiene and a vinyl heterocyclic nitrogen base such as 2-methyl-5-vinylpyridine. This propellant is produced by mixing a solid oxidant with the low Mooney viscosity copolymer, plus suitable curing agents, appropriate burning rate catalyst and low temperature oxidation inhibitor. The resulting mixture, which has the consistency of putty or other stiff paste, can be pressure molded or extruded into desired propellant configurations. This stiff paste is then converted into a material resembling automobile tire stock, having rubbery properties at temperatures as low as —90° F., by vulcanization.

Curing agents which can be used in vulcanizing the copolymers, utilized in the propellant grains and the coatings of this invention, include the well known curing agents used in the art such as vulcanizing agents including sulfur and sulfur compounds such as tetramethylthiuram disulfide, tetraethylthiuram disulfide and the like; accelerators such as the condensation product of mercaptobenzothiazole and cyclohexylamine, mercaptobenzothiazole, benzothiazyl disulfide, dithiocarbamates, zinc oxide, stearic acid, and the like; anti-oxidants such as hydroquinone benzylether, phenyl-β-naphthylamine, and the like; and other materials such as stiffeners, plasticizers and fillers.

If carbon black is to be used in the propellant composition, it is generally added as an aqueous slurry to the latex or alternatively carbon black can be milled directly into the dry polymer.

Commonly used combustion rate catalysts utilized in the propellant grains include metal ferrocyanides and ferricyanides. Ferric ferrocyanides, such as Prussian blue, Berlin blue, Hamburg blue, Chinese blue, Paris blue, 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. Milori blue is a pigment similar to Prussian blue but has 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, ammonium dichromate, and ferric oxide (rouge) can also be utilized.

The amount of solid oxidant employed in the admixture is usually a major amount of the total admixture, generally in the range from about 50 to about 90 percent by weight of the total admixture. If desired a minor amount of oxidant, less than 50 percent by weight can be employed.

The following objects will be attained by the aspects of the invention.

It is an object of this invention to provide an improved solid propellant as an article of manufacture.

It is another object of this invention to provide a coating for difficultly ignitable propellant charges so as to improve their ignition characteristics.

It is still another object to provide a method for improved ignition of solid propellants at atmospheric pressure.

It is another object to provide a novel composition for coating solid propellant charges.

Other objects and advantages will be apparent to one skilled in the art upon reading the disclosure of this invention.

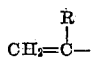
We have discovered that difficultly ignitable solid pro-

pellant charges can be satisfactorily ignited when they are coated with a mixture of a binder, such as synthetic or natural rubber, and ammonium perchlorate. The coating can be applied by spraying, by painting, by dipping or by any other means. The coating is usually applied so as to provide a coating thickness of from about 1/32 of an inch to 1/64 of an inch although the coating can be applied either thinner or thicker if it is so desired. The coating is cured by heating to drive off the solvent and to vulcanize and/or quaternize the polymeric material. The coating can be applied to the cured or uncured grain, however, it is preferred to apply the coating to the cured grain.

The binder used as a component of our novel propellant coating mixture is preferably synthetic or natural rubber dissolved in a solvent so as to produce a viscous liquid or such rubbery material can be a liquid copolymer such as a copolymer of 1,3-butadiene and 2-methyl-5-vinylpyridine, Thiokol, 1,3-butadiene and styrene, or other rubbery copolymer. The binder can, for example, be any of the copolymers disclosed in the hereinbefore referred to copending application.

The conjugated dienes employed in the practice of this invention are preferably conjugated diolefins which contain four to six inclusive carbon atoms per molecule, and include 1,3-butadiene, isoprene, piperylene, methylpentadiene, 2,3-dimethyl-1,3-butadiene, chloroprene and others. However conjugated dienes having more than 6, such as 8, carbon atoms per molecule may also be used. Furthermore various alkoxy, such as methoxy and ethoxy, and cyano derivatives of these conjugated dienes can also be used in the process of our invention.

The heterocyclic nitrogen bases, including the alkyl substituted bases, which are employed in the practice of our invention are those which are copolymerizable with a conjugated diene and include the



substituted nitrogen bases wherein R is a suitable substituent atom or group, e.g. a hydrogen atom or a hydrocarbyl group, such as an alkyl group. The vinyl-substituted heterocyclic nitrogen bases of the pyridine and quinoline series having only one vinyl substituent group and their various alkyl-substituted derivatives thereof are preferred. It is preferred however that the total number of carbon atoms in the nuclear substituted alkyl groups attached to any pyridine or quinoline unit be not greater than twelve. Furthermore in addition to vinyl-substituted pyridines and vinyl-substituted quinolines, the isopropenyl-substituted (i.e. a vinyl group having a methyl substituent in the alpha position) pyridines or quinolines may also be used. It is to be understood that mixtures of various conjugated dienes and mixtures of various copolymerizable heterocyclic bases may be employed in the practice of our invention together with, if desired up to about 50% by wt. preferably between 5 and 30% by wt. of the total monomeric material, of other copolymerizable materials, such as acrylonitrile.

The proportions of binder and ammonium perchlorate will usually be from 40 to 85 weight percent perchlorate and from 15 to 60 weight percent binder. A mixture of substantially equal parts by weight of ammonium perchlorate and binder is preferred.

When a binder containing a heterocyclic nitrogen compound, such as 2-methyl-5-vinylpyridine, is used, the liquid coating can be converted into a solid coating by quaternizing the mixture with the aid of a quaternizing agent such as alkyl halides, alkylene halide, and other known quaternizing agent. In some cases it may not be desirable to quaternize the coating compound, for example, those cases where evaporation of the rubber solvent provides the desired coating characteristics and in those cases where vulcanization is substituted for quaternization. After the coating is applied to the grain the coating is cured, usually by heating at a temperature in the range 30 to 175° C. for a time in the range of 30 minutes to 80 hours. Usually heating for 24 hours at 80° C. is sufficient for quaternization and vulcanization of most coating compositions.

The following examples are illustrative of our invention, however, our invention is not to be limited by these specific examples.

Example I

A low Mooney copolymer of 1,3-butadiene with 2-methyl-5-vinylpyridine, having a Mooney viscosity of 15–30, was prepared by emulsion polymerization at 50° C. using the following recipe:

	Parts by weight
1,3-butadiene	75
2-methyl-5-vinylpyridine	25
Sodium soap flakes	5
Water	180
Potassium persulfate	0.3
Mercaptan blend [1]	5

[1] A blend of tertiary C_{12}, C_{14}, and C_{16} aliphatic mercaptans in a ratio of 3 : 1 : 1 parts by weight.

Polymerization was effected in the conventional manner and gave a 95 percent conversion in eight hours.

A binder component for a propellant was prepared by combining the following materials:

	Parts by weight
Butadiene-MVP copolymer	100
Furnace carbon black	20
Flexol TOF [1]	20
Benzotrichloride	6.6
Sulfur	1.75
Butyl eight [2]	2
Zinc oxide	5
Aerosol OT [3]	1

[1] Tri-2-ethylhexyl phosphate.
[2] Dithiocarbamate.
[3] Sodium dioctyl sulfosuccinate.

A propellant charge was prepared by combining 75 parts by weight of ammonium nitrate, 25 parts by weight of the above binder and one part by weight of rouge. The charge was compression molded.

A coating material was prepared by dissolving 10 parts, based on the butadiene/MVP copolymer, of the above binder composition in 90 parts of methylcyclohexane. Ammonium perchlorate was added while stirring so as to give a uniform mixture of about 50/50 ammonium perchlorate/butadiene/MVP copolymer. A thin coating was applied to the surface of a propellant charge, described above, by painting and the coating was cured for 24 hours at 80° C.

The propellant charge was tubular in shape, the outside diameter about 3 in., the inside diameter about 1 in., and the length about 5 in. The charge was fired in a test rocket motor. Combustion chamber pressure was recorded during firing and the charge was ignited at atmospheric pressure.

A charge without coating was fired and more than one second was required to reach full thrust. The coated charge reached full thrust in less than 0.1 second.

Example II

A second binder material was prepared by compounding the copolymer described in Example I as follows:

	Parts by weight
Butadiene-MVP copolymer	100
Furnace carbon black	20
Flexol TOF	20
Benzotrichloride	6.6
Butyl eight	2
Sulfur	1.75
Zinc oxide	5
Aerosol OT	1
Triphenylphosphite	1

A propellant charge was compounded by combining 75 parts by weight of ammonium nitrate, 25 parts by weight of the above binder and 2 parts by weight of rouge. The propellant charge was molded as described in Example I and was coated with a material prepared by mixing equal parts by weight of Thiokol LP–3 and ammonium perchlorate. A coating of approximately 1/32 inch thick was applied to the entire charge and was cured by heating to 80° C. for 24 hours. The coating was removed from the ends before firing as described in Example I. Full thrust was reached in less than 0.1 second using the 50-50 Thiokol LP–3/ammonium perchlorate coating. The charge burned smoothly throughout the firing period. A charge fired without the coating required over one second to reach full thrust. Thiokol LP–3 is commercially available as a syrupy liquid and is described as a difunctional mercaptan having an average molecular weight of 1000.

The results of the examples show that the coating material of this invention was remarkably effective in reducing ignition delay in firing the propellant charges.

The coating can be applied to propellant grains of any size or shape and is particularly effective in promoting uniform burning rate when a rocket charge is composed of a plurality of propellant grains.

In some cases it may be desirable to remove the coating from portions of the grain such as from one end or both ends so as to control ignition characteristics. It is also possible to control ignition characteristics by varying the coating thickness.

Variations and modifications are possible within the scope of the invention, the essence of which is the discovery that a coating of a mixture of rubbery material and ammonium perchlorate reduces ignition delay of a solid propellant charge and promotes uniform burning during the firing period.

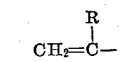
That which is claimed is:

1. A method for improving the ignition characteristics of a difficultly ignitable solid propellant charge which comprises coating said charge with an admixture comprising about 15 to 60 weight percent of rubber and about 40 to 85 weight percent of ammonium perchlorate.

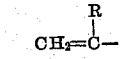
2. A method for improving the ignition characteristics of a composite propellant comprising a major amount of ammonium nitrate and a minor amount of a solid polymeric quaternary ammonium compound which comprises coating said propellant with a continuous film of about 40 to 85 weight percent of a mixture of ammonium perchlorate and about 15 to 60 weight percent of a butadiene/methylvinylpyridine copolymer; and curing said coating at a temperature in the range of 30 to 175° C. for a time in the range of 30 minutes to 80 hours.

3. A method for improving the ignition characteristics of a difficultly ignitable solid propellant which comprises coating said propellant with a continuous film of an admixture comprising about 15 to 60 weight percent of rubber and about 40 to 85 weight percent of ammonium perchlorate; and removing a predetermined portion of said coating.

4. A method for preparing a solid propellant having improved ignition characteristics at atmospheric pressure which comprises applying, to a propellant grain comprised of a major amount of ammonium nitrate and a copolymer of a conjugated diene having up to 8 carbon atoms per molecule, and a



substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, and alkyl substituted derivatives thereof wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 12 and wherein R is selected from the group consisting of hydrogen and an alkyl radical and where said

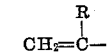


group is attached to a nuclear carbon atom, a continuous coating of a thickness of 1/64 inch to 1/32 inch of a mixture of about 100 parts by weight of each of ammonium perchlorate and a copolymer of butadiene with 2-methyl-5-vinylpyridine; from 5 to 10 parts by weight of benzotrichloride; and about 900 parts by weight of methylcyclohexane; and curing the resulting coated grain for about 24 hours at about 80° C.

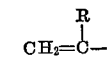
5. A solid propellant comprising an intimate admixture of from 50 to 90 weight percent of ammonium nitrate and from 10 to 50 weight percent of a solid 1,3-butadiene-N-alkyl vinylpyridine copolymer coated with a continuous film from 1/64 to 1/32 of an inch thick of an admixture of about 50 weight percent of a copolymer comprising from 50 to 90 weight percent of 1,3-butadiene and 10 to 50 weight percent of 2-methyl-5-vinylpyridine, and about 50 weight percent of ammonium perchlorate.

6. A coating for a difficultly ignitable solid propellant grain comprising a continuous bonded coating of a uniform mixture of equal parts of ammonium perchlorate and rubber.

7. A method for improving the ignition characteristics of a composite propellant comprising a major amount of ammonium nitrate and a copolymer of a conjugated diene having up to 8 carbon atoms per molecule, and a

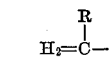


substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, and alkyl substituted derivatives thereof wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 12 and wherein R is selected from the group consisting of hydrogen and an alkyl radical and where said

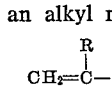


group is attached to a nuclear carbon atom which comprises coating said propellant with a continuous film of a mixture of about 40 to 85 weight percent of ammonium perchlorate and about 15 to 60 weight percent of a butadiene-methylvinylpyridine copolymer; and curing said coating at a temperature in the range of 30 to 175° C. for a time in the range of 30 minutes to 80 hours.

8. A method for improving the ignition characteristics of a composite propellant comprising about 40 to 85 weight percent of an inorganic oxidizing salt and a copolymer of a conjugated diene having up to 8 carbon atoms per molecule, and a



substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, and alkyl substituted derivatives thereof wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 12 and wherein R is selected from the group consisting of hydrogen and an alkyl radical and where said



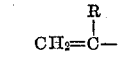
group is attached to a nuclear carbon atom which comprises coating said propellant with a continuous film of about 40 to 85 weight percent of a mixture of about 40 to 85 weight percent of ammonium perchlorate, from about 15 to 60 weight percent of a butadiene-methylvinylpyridine copolymer, and vulcanizing agents; and curing said coating at a temperature in the range of 30° C. to 175° C. for a time in the range of 30 minutes to 80 hours.

9. A solid propellant comprising an intimate admixture of from 50 to 90 weight percent of ammonium nitrate and from 10 to 50 weight percent of a solid 1,3-butadiene-N-alkyl vinylpyridine copolymer coated with a continuous film from 1/64 to 1/32 of an inch thick of an admixture of about 50 weight percent of natural rubber and about 50 weight percent of ammonium perchlorate.

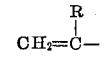
10. A solid propellant comprising an intimate admixture of from 50 to 90 weight percent of ammonium nitrate and from 10 to 50 weight percent of a solid 1,3-butadiene-N-alkyl vinylpyridine copolymer coated with a continuous film from 1/64 to 1/32 of an inch thick of an admixture of about 50 weight percent of a copolymer of 1,3-butadiene and styrene, and about 50 weight percent of ammonium perchlorate.

11. A solid propellant comprising an intimate admixture of from 50 to 90 weight percent of ammonium nitrate and from 10 to 50 weight percent of a solid 1,3-butadiene-N-alkyl vinylpyridine copolymer coated with a continuous film of from 1/64 to 1/32 of an inch thick of an admixture of about 50 weight percent of a copolymer of 1,3-butadiene and 2-vinylpyridine, and about 50 weight percent of ammonium perchlorate.

12. A solid propellant comprising an intimate mixture of from 50 to 90 weight percent of a solid inorganic oxidizing salt and from 10 to 50 weight percent of a copolymer of a conjugated diene having up to 8 carbon atoms per molecule and a



substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, and alkyl substituted derivatives thereof wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 12 and wherein R is selected from the group consisting of hydrogen and an alkyl radical and wherein



group is attached to a nuclear carbon atom, coated with a continuous film of 1/64 to 1/32 of an inch thick of an admixture of about 15 to 60 weight percent of rubber and about 40 to 85 weight percent of ammonium perchlorate.

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2,402,020 Cislak et al. ---------- June 11, 1946

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

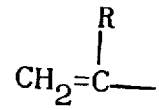
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May 1, 1962

Homer M. Fox et al.

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

Column 5, line 47, strike out "of a mixture" and insert the same after "film" in line 46, same column 5; column 6, lines 49 to 51, the formula should appear as shown below instead of as in the patent:



column 8, line 12, for "of", first occurrence, read -- from --.

Signed and sealed this 9th day of October 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents