United States Patent Office

2,941,352

Patented June 21, 1960

2,941,352

SOLID COMPOSITE PROPELLANTS WITH BURNING RATE CATALYST

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No Drawing. Filed Feb. 4, 1957, Ser. No. 638,176

8 Claims. (Cl. 60—35.4)

This invention relates to solid propellants. In one aspect it relates to an improved method for producing solid propellant mixtures comprising a solid oxidant, a rubbery binder material and a burning rate catalyst. In another aspect the invention relates to a novel composition employed in the manufacture of solid propellant mixtures which provides an improvement in the compounding of solid propellant mixtures. In still another aspect it relates to a simplified and improved sequence of steps employed in the manufacture of solid propellants.

Recently it has been discovered that superior solid propellant mixtures are obtained comprising a solid oxidant such as ammonium nitrate or ammonium perchlorate and a rubbery binder 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 solid propellant mixtures of the type hereinbefore disclosed, the ratio of oxidant to binder is usually very high, often about 5 to 9 parts by weight of oxidant to one part by weight of binder material. It is necessary that the rubbery binder of such propellant mixtures be the continuous phase in which the oxidant is dispersed in order to obtain satisfactory consolidation so that upon curing a solid material of substantial structural strength will be obtained. Heretofore, one of the difficulties encountered in the manufacture of propellants of this type has been that of loss of a continuous phase whereby the binder forms a discontinuous phase in the oxidizer. When the continuous phase is lost in this manner, the batch cannot be used to prepare a propellant charge and must be discarded or reprocessed in some manner. An additional difficulty attnedant with a mixture having a tendency toward loss of continuous phase is that the mixing time required to obtain a satisfactory product is greatly extended.

In copending application Serial No. 475,000, filed December 13, 1954, by H. G. Cutforth, there is described a method for preparing solid propellant mixtures of the nature contemplated in this invention which comprises dry blending the burning rate catalyst and the solid oxidant prior to its incorporation in the rubber binder material. This procedure resulted in improved results over the prior art methods of mixing the dry solid oxidant and the rubbery binder over the procedures known heretofore. This procedure, however, requires that both the solid oxidant and the burning rate catalyst be dry when blended together and the burning rate catalyst, which is Milori blue, is subject to dusting during the mixing operation with the result that the equipment and the operators are continually subjected to coloring by the blue dust evolved from the mixing operation.

It is therefore an object of this invention to provide an

improved method for producing solid propellants. It is also an object of this invention to provide a sequence of steps whereby the drying step with respect to the solid oxidant and the burning rate catalyst is eliminated in the production of solid propellant mixtures. Another object of this invention is the provision of a method for producing solid propellant mixtures wherein the step of dry blending the solid oxidant and the burning rate catalyst is eliminated. It is still another object of this invention to provide a novel composition of ingredients which facilitates the incorporation of a solid oxidant into a rubbery binder. Other objects and advantages of this invention will be apparent to one skilled in the art upon studying this disclosure.

Broadly, the invention relates to an improved method for the manufacture of solid propellants by incorporating a paste comprising a complex cyanide of iron, which is prepared in the presence of a small amount of naphthenic acid, and a plasticizer, into the rubbery binder prior to incorporation therein of the solid oxidant. A surface active agent is preferably utilized in preparing the paste and is removed in drying the paste. The invention also relates to a novel composition comprising a complex cyanide of iron prepared in the presence of a small amount of naphthenic acid and a plasticizer such as dibutoxyethoxyethyl formal, monoamylbiphenyl, benzophenone, liquid polybutadiene, and the like. Dibutoxyethoxyethyl formal is the preferred plasticizer and it has been found that the commercial grade of this material sometimes contains impurities boiling at less than 190° F., therefore, this material preferably is distilled at a temperature of about 190° F. and atmospheric pressure to remove such impurities. If other plasticizers are used it should be determined that they contain no materials boiling or vaporizing at a temperature below about 190° F.

Oxidants applicable in preparing the solid propellants applicable to the process of this invention are those oxygen-containing solids which readily give up oxygen and include ammonium nitrate, ammonium perchlorate and various other perchlorates, chlorates, dichromates, chromates, and the like. The average particle size of a finely divided oxidant suitable for blending with a catalyst so as to obtain the improvements of this invention should be less than 200 microns and can be from 60 to 200 microns. The amount of solid oxidant uilized is usually a major amount of the total composition and is generally in the range between 50 and 90 weight percent of the total propellant composition. If desired, however, less than 50 weight percent of the oxidant can be used.

The catalysts which can be used in the practice of this invention include iron cyanide complexes such as Milori blue, Prussian blue, Chinese blue, and the like, ammonium dichromate, potassium dichromate, ferric oxide, lead oxide, and the like. The average particle size of the finely divided catalyst which can be used to obtain the improvements of this invention should be less than 40 microns and can be from 0.02 to 40 microns. The amount of catalyst used in preparing propellant compositions according to he method of this invention is usually in the ranged of 7 to 200 parts by weight of oxidant per part by weight of catalyst. The preferred catalyst for the practice of this invention is Milori blue, which is a highly colored pigment material similar to Prussian blue prepared by the oxidation of a paste of potassium ferrocyanide and ferrous sulfate in the presence of a small amount of naphthenic acid. Electron micrographs at 50,000× of this preferred catalyst show the ultimate particles to be uniform in size, apparently spherical in shape and strung together in short chains. Similar micrographs of Milori blue prepared in the absence of naphthenic acid show ultimate particles which have a more blocky, crystalline appearance and a wide range of ulti-

mate particle size. The catalyst is mixed with 40 to 50 weight percent of plasticizer so as to form a paste which is added to the rubbery binder prior to incorporation of the solid oxidant therein. The preferred method for preparing the paste is to mix the plasticizer with the wet catalyst presscake recovered from the oxidation step, and this is cenveniently accomplished in the presence of a surface active agent capable of displacing water from the catalyst surface and rendering the surface compatible with the plasticizer. Such surface active agents include Ethomeens (ethylene oxide substituted alkyl amines marketed by Armour and Co.). Other wetting agents can be used and it is preferred that the wetting agent be such that it will be removed during the drying step.

The copolymers which are used to bind the materials of the solid propellants comprise a conjugated diene containing from 4 to 8 carbon atoms per molecule such as butadiene, isoprene, piperylene, methylpentadiene, chloroprene, and the like copolymerized with a polymerizable heterocyclic nitrogen base such as the vinyl-substituted pyridines, vinyl-substituted quinolines and various alkyl-substituted derivatives of these compounds such as 2-methyl-5-vinylpyridine (MVP), 2-vinylpyridine, 2-vinylquinoline and the like. The copolymers can be prepared by any suitable method, e.g., emulsion polymerization. It is often desirable to incorporate carbon black in the copolymer during its preparation. The addition of carbon black is accomplished by conventional methods, such as adding the carbon black to the latex prior to coagulation to form a masterbatch, and the amount of carbon black can be from 0 to 35 parts of black per 100 parts of copolymer. In the preparation of the copolymers, the amount of conjugated diene will be at least 50 parts by weight per 100 parts of the monomer mixture and the heterocyclic nitrogen base component will be in the range 5 to 50 parts. While the invention is described herein with particular respect to polymers in which a heterocyclic nitrogen base is included, other rubbery polymers, such as butadiene-styrene copolymer, are also applicable.

Compounding agents are incorporated into the copolymer in producing the rubbery binder of the propellant compositions prepared according to the process of this invention. Compounding agents include vulcanization agents, quaternization agents, vulcanization accelerators, softeners, stabilizers such as antioxidants, surface active agents, etc.

The Milori blue prepared in the presence of naphthenic acid will contain naphthenic acid in the range of about 1½ to about 2½ weight percent.

The composition of a typical propellant manufactured by the process of this invention is shown in Table I but it is to be understood that the composition is exemplary and is not to be construed as limiting the invention.

Table I

Ingredient	Parts Per 100 Parts Copolymer	Weight Percent
Butadiene-methylvinylpyridine copolymer	100	12–25
Filler (carbon black)	10–30	
Plasticizer (di-butoxyethoxyethyl formal)	10–30	
Burning rate catalyst (Milori blue)	10–30	
Oxidant (ammonium nitrate)		88–75

Auxiliary ingredients may also be added to the copolymer binder composition as listed in Table II.

Table II

Ingredient	Parts/100 Parts Binder
Wetting agent	0.3
Antioxidant	0.3
Sulfur	0.3
Cure accelerators	0.3

As a specific embodiment of the invention the preparation of a solid propellant will be described having the composition shown in Table III.

Table III

Ingredient	Wt. Percent
Ammonium nitrate	81.05
Butadiene-methylvinylpyridine copolymer (90/10)	11.00
Dibutoxyethoxyethyl formal	2.21
Furnace carbon black	2.48
Flexamine (A physical mixture containing 65% of a complex diarylaminoketone reaction product and 35% N,N'-diphenyl-p-phenylenediamine	0.33
Magnesium oxide	0.49
Milori blue	1.94

The butadiene-methylvinylpyridine copolymer containing the carbon black was received as a masterbatch from the supplier. The masterbatch was masticated and the plasticizer and Milori blue were added in the form of a previously prepared paste. The paste was prepared by admixing dibutoxyethoxyethyl formal with Milori blue prepared in the presence of naphthenic acid and containing about 2 weight percent naphthenic acid in the proportions shown in Table III. A wetting agent was employed in preparing the paste and was removed substantially with the water in a vacuum drying step. Some of the water separated from the plate and was decanted during the mixing step. The flexamine and magnesium oxide were added to the copolymer binder composition during mastication and mastication was continued until the temperature of the binder had risen to the range of 130 to 155° F. The oxidizer was then added in four increments with continuous mastication of the mixture without loss of continuous phase of the binder material.

After thorough mastication of the entire composition the mixture was extruded in the form of propellant grains and was cured at a temperature of about 170° F. for a period of 18 hours.

Propellant grains which were prepared according to the above procedure were fired and the results were compared with results obtained by firing propellant grains prepared according to the procedure of the prior art. All factors, other than the procedural steps of preparing the propellant composition, were held constant. The data obtained from firing these propellant grains are tabulated in Table IV.

Table IV

Properties	Control Grains	Grains Made With Paste
Burning rate r at 1,000	0.148	0.150.
c*	4040	4014.
I_{sp}	188	188.
Process Ability	Good	Good.
Physical Appearance of Grain	Smooth	Smooth.
Catalyst Dispersion	Satisfactory	Satisfactory.

The above data show that the ballistic parameters are substantially equal and that the processability and other characteristics of these compositions are also substantially equal and therefore the process according to this invention provides a definite advantage in the preparation of the composition by the elimination of one step in the process, namely that of dry blending the catalyst and the oxidant, and also avoids dusting of the personnel and equipment with the highly colored burning rate catalyst.

Reasonable variations and modifications are possible within the scope of the disclosure of this invention, the essence of which is the provision of an improved procedure for the preparation of solid propellants by incorporating the burning rate catalyst together with the plasticizer into the binder material and then incorporating the solid oxidant into the binder material. Further im-

provements are achieved by preparing a paste of the burning rate catalyst and the plasticizer; removing materials from the di-butoxyethoxyethyl formal which vaporizes at a temperature below 190° F.; and preparing Milori blue as a burning rate catalyst in the presence of a small amount of naphthenic acid.

That which is claimed is:

1. In the method of developing thrust wherein a solid propellant charge contained in a combustion chamber of a rocket motor is ignited and then burned with the evolution of combustion gases which are exhausted from said combustion chamber, the step which comprises burning in said combustion chamber a propellant charge comprising: as a base propellant, about 50 to 90 weight percent of an inorganic oxidizing salt; and about 50 to about 10 weight percent of a binder comprising a copolymer of a conjugated diene having 4 to 8 carbon atoms per molecule and at least one

$$CH_2=\overset{|}{C}-R$$

substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, an alkyl substituted pyridine and an 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, 0 to 35 parts of carbon black per 100 parts of copolymer, 10 to 30 parts by weight per 100 parts copolymer of a plasticizer selected from the group consisting of di-butoxyethoxyethyl formal, monoamylbiphenyl, benzophenone, and liquid polybutadiene, and 10 to 30 parts by weight per 100 parts copolymer of Milori blue prepared in the presence of a sufficient amount of naphthenic acid so that 1½ to 2½ weight percent naphthenic acid remains in the Milori blue whereby the particles of Milori blue are spherical in shape, strung together in short chains, and are uniform in size in a range of 0.02 to 40 microns.

2. A composition consisting essentially of 40 to 60 weight percent Milori blue prepared in the presence of a sufficient amount of naphthenic acid so that 1½ to 2½ weight percent naphthenic acid remains in the Milori blue; and 40 to 60 weight percent di-butoxyethoxyethyl formal.

3. A composition consisting essentially of 40 to 60 weight percent Milori blue prepared in the presence of a sufficient amount of naphthenic acid so that 1½ to 2½ weight percent naphthenic acid remains in the Milori blue; and 40 to 60 weight percent of a plasticizer selected from the group consisting of di-butoxyethoxyethyl formal, monoamylbiphenyl, benzophenone, and liquid polybutadiene.

4. A solid propellant composition consisting essentially of about 50 to 90 weight percent of an inorganic oxidizing salt; and about 50 to about 10 weight percent of a binder consisting essentially of a copolymer of a conjugated diene having from 4 to 8 carbon atoms per molecule and at least one

$$CH_2=\overset{|}{C}-R$$

substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, an alkyl substituted pyridine and an 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, 0 to 35 parts of carbon black per 100 parts copolymer, and 10 to 30 parts by weight per 100 parts copolymer of Milori blue prepared in the presence of a sufficient amount of naphthenic acid so that 1½ to 2½ weight percent naphthenic acid remains in the Milori blue whereby the particles of Milori blue are spherical in shape, strung together in short chains, and are uniform in size in a range of 0.02 to 40 microns.

5. A solid propellant composition consisting essentially of 50 to 90 weight percent of an inorganic oxidizing salt; and about 50 to about 10 weight percent of a binder consisting essentially of a copolymer of a conjugated diene having 4 to 8 carbon atoms per molecule and at least one

$$CH_2=\overset{|}{C}-R$$

substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, an alkyl substituted pyridine and an 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, 0 to 35 parts of carbon black per 100 parts of copolymer, 10 to 30 parts by weight per 100 parts copolymer of a plasticizer selected from the group consisting of di-butoxyethoxyethyl formal, monoamylbiphenyl, benzophenone, and liquid polybutadiene, and 10 to 30 parts by weight per 100 parts copolymer of Milori blue prepared in the presence of a sufficient amount of naphthenic acid so that 1½ to 2½ weight percent naphthenic acid remains in the Milori blue whereby the particles of Milori blue are spherical in shape, strung together in short chains, and are uniform in size in a range of 0.02 to 40 microns.

6. An improved method for preparing an extrudable solid propellant composition comprising an inorganic solid oxidizing salt, a binder comprising a copolymer of a conjugated diene having 4 to 8 carbon atoms per molecule and at least one

$$CH_2=\overset{|}{C}-R$$

substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, an alkyl substituted pyridine and an 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, Milori blue prepared in the presence of a sufficient amount of naphthenic acid so that 1½ to 2½ weight percent naphthenic acid remains in the Milori blue, and a rubber plasticizer, which comprises first admixing the Milori blue and plasticizer to form a paste containing about 40 to 60 weight percent Milori blue and about 40 to 60 weight percent plasticizer; then admixing said paste with the copolymer binder; and then admixing the solid oxidant with the plasticized binder.

7. In the process of making an extrudable solid propellant composition comprising an inorganic solid oxidizing salt, a binder comprising a copolymer of a conjugated diene having from 4 to 8 carbon atoms per molecule and at least one

$$CH_2\overset{|}{C}-R$$

substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, an alkyl substituted pyridine and an 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, Milori blue prepared in the presence of a sufficient amount of naphthenic acid so that 1½ to 2½ weight percent naphthenic acid remains in the Milori blue, and a rubber plasticizer, the improvement comprising first admixing Milori blue and plasticizer to form a paste containing about 40 to 60 weight percent Milori blue and about 40 to 60 weight percent plasticizer; then admixing the paste and the copolymer binder; and then admixing the solid oxidant with the copolymer binder so that the binder forms the continuous phase in the resulting composition.

8. The process of claim 7 wherein the oxidizing salt is ammonium nitrate; the binder is a copolymer of buta-

diene and methylvinylpyridine; and the plasticizer is dibutoxyethoxyethyl formal.

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