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MANUFACTURE OF SOLID PROPELLANTS

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This invention relates to solid propellant mixtures. In one of its more specific aspects it relates to an improved method for producing solid propellant mixtures comprising a solid oxidant and a rubbery binder material. In still another aspect the invention relates to a particular sequence of steps employed in the manufacture of solid propellant mixtures comprising a solid oxidant and a rubbery binder material whereby improved results are obtained.

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 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, and in copending application Serial No. 463,828, filed October 21, 1954, by H. M. Fox.

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 attendant 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.

Each of the following objects will be attained by the aspects of this invention.

It is an object of this invention to provide an improved method for producing solid propellants.

Another object of this invention is to provide a sequence of steps whereby the production of a solid propellant comprising a solid oxidant and a rubbery material is accomplished in a shorter time.

It is also an object of this invention to provide a sequence of steps for producing a solid propellant comprising a solid oxidant and a rubbery material whereby loss of continuous phase of the binder component of the solid propellant is avoided.

It is still another object to provide a method for producing uniform solid propellants.

Other objects and advantages of this invention will be

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apparent to one skilled in the art upon studying this disclosure.

I have discovered that in the preparation of a solid propellant comprising a solid oxidant and a rubbery binder that if the finely divided oxidant is dry-blended with the finely divided burning rate catalyst prior to being mixed with the rubbery binder, the problem of loss of continuous phase of the binder does not arise, and the time required for mixing the oxidant with the binder is greatly reduced. While it is possible to mix the catalyst and the oxidant together prior to grinding, it is preferred to grind these components separately before mixing them together.

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 utilized 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 milori blue, Prussian blue, ammonium dichromate, potassium dichromate, ferric oxide, lead dioxide, and the like. The average particle size of a finely divided catalyst which can be blended with an oxidant 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 utilized in preparing propellant compositions according to the method of this invention is usually in the range of 7 to 200 parts by weight of oxidant per part by weight of catalyst. The preferred catalyst for propellants of this type 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. Grinding such highly colored and finely divided material with the oxidant raises an operating problem in that the operating environment and the operators themselves are exposed to colored dusts emitting from the grinder. These colored dusts, in addition to being annoying, may have toxic effects on the operators when exposed to these dusts for considerable periods of time. The grinding of the oxidant with the highly active combustion catalysts can be a hazardous operation and should be avoided. The degree of hazard involved in such grinding operation depends upon the oxidant and catalyst which are being used. Thus, while grinding an ammonium nitrate oxidant with a catalyst usually offers little hazard, the grinding of a perchlorate oxidant with a catalyst can be extremely hazardous.

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 coagula-

tion 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 a 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.

While it has not been discovered just what effect the dry-blending of the catalyst with the oxidant has upon the oxidant which causes the improvements of this invention, it has been discovered that a number of catalyst and oxidant combinations show the advantages of this invention when they are dry blended together prior to being mixed with the rubbery binder.

In the practice of this invention, any one of the catalysts described above or a mixture of such catalysts can be dry-blended with any one of the oxidants described above or a mixture of such oxidants prior to the incorporation of these catalyst-oxidant blends into a rubbery binder to form a propellant mixture. This process of dry-blending results in more rapid incorporation of the oxidant into the rubbery binder, shorter overall mixing time, and elimination of having to discard batches because of lack of consolidation resulting from loss of continuous binder phase. Blending of the oxidant and catalyst can be accomplished by conventional methods of dry mixing.

The following examples illustrate the invention but are not to be construed to limit the invention.

EXAMPLE I

A propellant was prepared with a binder composition according to Table I using the procedure set forth following Table I.

Table I

Components	Parts by Weight
Copolymer black masterbatch ¹	110
Benzophenone.....	8
Pentaryl A (amylbiphenyl).....	8
Sulfur.....	1.75
Zinc Oxide.....	3
Aerosol OT (dioctyl ester of sodium sulfosuccinic acid).....	1
Flexamine (a physical mixture containing 65% of a complex diarylamineketone reaction product and 35% N,N'-di-phenyl-p-phenylenediamine).....	3

¹ Copolymer prepared by emulsion polymerization of a monomer mixture comprising 90 parts by weight butadiene and 10 parts by weight 2-methyl-5-vinylpyridine. Copolymer masterbatched with 10 parts by weight medium abrasion furnace black per 100 parts by weight copolymer.

The copolymer black masterbatch was kneaded for 5 minutes in a Baker-Perkins mixer. The sulfur, zinc oxide, Aerosol OT and Flexamine were then added and mixed for 3 minutes after which the benzophenone and Pentaryl A were added and the entire batch mixed for 50 minutes.

Approximately 743 grams of the binder composition prepared as described above was placed in a Baker-Perkins mixer and kneaded for 5 minutes under a vacuum of 29.5 inches of mercury. To this copolymer was then added 33.2 grams of epichlorohydrin, and the mixture was then mixed in the mixer for 7 minutes. A total of 3712.5 grams of finely divided (average diameter 40 microns) ammonium nitrate was added in increments. About 500

grams of ammonium nitrate was first added and mixed under a vacuum lid, but with no vacuum, for 9 minutes after which about 600 grams of ammonium nitrate was added and mixed for 21 minutes. About 1000 grams of ammonium nitrate was then added and mixed for 34 minutes, after which an additional 1500 grams of ammonium nitrate was added and mixed for 5 minutes. Oxidant and binder were mixed until complete incorporation was obtained after each increment addition. The remaining ammonium nitrate was then added and mixed for one minute. The mixture was mixed under the vacuum lid, with no vacuum, for an additional 5 minutes but the ammonium nitrate had not been incorporated into the binder at this point. Ninety grams of milori blue having an average particle size of 0.03 to 0.04 micron was then added to the mixture, after which mixing was continued for 6 minutes. At this point the oxidant was found to be incorporated into the binder. 11.1 grams of Butyl-Eight, a dithiocarbamate type rubber accelerator, was then added and the batch was mixed under the compression ram for 15 minutes. The mixture was then mixed under the vacuum lid for an additional 15 minutes, 5 of which took place under a vacuum of 29.5 inches of mercury. The propellant mixture was then removed from the mixer. The temperature of this mixture at the time of the removal from the mixer was 153° F. The consolidation of the ammonium nitrate and the binder was satisfactory. The overall time for this run, not including preparation of the binder, was 123 minutes, while the time required for the addition of oxidant was 69 minutes.

After the mixing operation was completed the propellant composition was extruded into grains and cured to produce the solid propellant product.

Of the first 18 runs made, using the procedure of this example, 4 runs were lost due to lack of incorporation of the ammonium nitrate and the copolymer binder. The average time required for the preparation of the 14 successful runs was about 130 minutes.

EXAMPLE II

A binder composition was prepared using the recipe and the procedure of Example I with the exception that the epichlorohydrin was added just prior to the addition of the benzophenone and Pentaryl A. The reason that the epichlorohydrin was not added to the mix prior to the addition of benzophenone and Pentaryl A in Example I was because the mix was not used immediately and the epichlorohydrin is a quaternizing agent which causes solidification of the copolymer.

A mixture of 3712.5 grams of finely divided (average 40 microns) ammonium nitrate and 90 grams of milori blue having an average particle size of 0.03 to 0.04 micron, were then dry-blended together and added to approximately 778 grams of the binder composition in increments substantially as in Example I. These increments were mixed into the copolymer binder under the vacuum lid, but with no vacuum until incorporation was obtained. The addition and mixing of the oxidant-catalyst blend required 10 minutes, and after a 2 minute waiting period 11.1 grams of Butyl-Eight was added to the mixture. The propellant mixture was then mixed for 15 minutes under the compression ram at atmospheric pressure and was then mixed under the vacuum lid for an additional 10 minutes under a vacuum of 26 inches of mercury. The final temperature of the mix was 150° F. The incorporation of the oxidant and the copolymer binder was satisfactory. The overall time required for this run was 53 minutes, while the time required for the addition of ammonium nitrate was 10 minutes.

Fourteen runs were prepared by this procedure, and none of the runs was lost due to lack of incorporation of the oxidant and the binder. The average time required for preparation of these 14 runs was 50 minutes.

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EXAMPLE III

A propellant composition was prepared using a binder composition as set forth in Table II according to the procedure which follows.

Table II

Components	Parts by Weight
Copolymer black masterbatch ¹	120
Benzophenone.....	10
Pentaryl A.....	10
Sulfur.....	1.75
Zinc Oxide.....	3
Aerosol OT.....	1
Flexamine.....	3

¹ Copolymer prepared by emulsion polymerization of a monomer mixture comprising 90 parts by weight butadiene and 10 parts by weight 2-methyl-5-vinylpyridine. Copolymer masterbatched with 20 parts by weight medium abrasion furnace black per 100 parts by weight copolymer.

The rubber-black masterbatch was kneaded for 10 minutes in a Baker-Perkins mixer. The Flexamine, zinc oxide, sulfur, Aerosol OT, and benzophenone were added to the masterbatch and mixed for 3 minutes. The Pentaryl A was then added to the mixture and mixed for 2 minutes. A mixture of 3464 grams of finely divided (average particle size 40 microns) ammonium nitrate and 168 grams of ammonium dichromate (average particle size 20 microns), prepared by dry-blending the two materials together, was added to 726 grams of the copolymer mixture in increments substantially as in Example I and mixed under the vacuum lid, but with no vacuum. After a 5 minute waiting period, 9.77 grams of Butyl-Eight were added and the mixture mixed for 15 minutes under the compression ram at a pressure of 40 p.s.i. Mixing was then continued for an additional 10 minutes, 5 of which were under atmospheric pressure and 5 of which were under a vacuum of 29 inches of mercury. After a 5 minute period the mixture was removed from the mixer. The final temperature of the mixture was 150° F., and the consolidation of the ammonium nitrate and the binder composition was satisfactory. The overall time for the run was 82 minutes, while the time required for the addition of the ammonium nitrate was 18 minutes.

EXAMPLE IV

A propellant composition was prepared using a binder composition as set forth in Table III according to the procedure which follows.

Table III

Components	Parts by Weight
Copolymer black masterbatch ¹	120
Benzophenone.....	20
Sulfur.....	0.75
Zinc Oxide.....	3
Flexamine.....	3

¹ Copolymer prepared by emulsion polymerization of a monomer mixture comprising 90 parts by weight butadiene and 10 parts by weight 2-methyl-5-vinylpyridine. Copolymer masterbatched with 20 parts by weight medium abrasion furnace black per 100 parts by weight copolymer.

The rubber-black masterbatch was kneaded for 10 minutes in a Baker-Perkins mixer under a vacuum of 29 inches of mercury. The benzophenone, sulfur, zinc oxide, and Flexamine were added to the masterbatch and mixed for 3 minutes. A mixture of 2730 grams of finely divided ammonium nitrate, 756 grams of finely divided ammonium perchlorate and 168 grams of finely divided ammonium dichromate, prepared by dry-blending the materials together, was added to 714.3 grams of the copolymer mixture in increments substantially as in Example I and mixed under the vacuum lid, but with no vacuum. After a 3 minute waiting period, 4.84 grams of N,N-dimethyl tertiarybutyl sulfonyl dithiocarbamate were added and the mixture mixed for 15 minutes under the

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compression ram at a pressure of 32 p.s.i. Mixing was then continued for 15 minutes under a vacuum of 29+ inches of mercury. The final temperature of the mixture was 130° F. and the incorporation of the oxidant and binder was satisfactory. The overall time for the run was 55 minutes, while the time required for the addition of the oxidant mixture was 7 minutes.

EXAMPLE V

A propellant composition was prepared using a binder composition as set forth in Table IV according to the procedure which follows.

Table IV

Components	Parts by Weight
Copolymer black masterbatch ¹	120
Flexamine.....	3
Sulfur.....	1.75
Aerosol OT.....	1
Benzophenone.....	10
Pentaryl A.....	10
Epichlorohydrin.....	6

¹ Copolymer prepared by emulsion polymerization of a monomer mixture comprising 90 parts by weight butadiene and 10 parts by weight 2-methyl-5-vinylpyridine. Copolymer masterbatched with 20 parts by weight medium abrasion furnace black per 100 parts by weight copolymer.

The rubber-black masterbatch was kneaded for 5 minutes under a vacuum of 29 inches of mercury in a Baker-Perkins mixer. The sulfur, zinc oxide, Aerosol OT, Flexamine and benzophenone were added to the masterbatch and mixed for 2 minutes. The Pentaryl A and epichlorohydrin was then added to the mixture and mixed for one minute. A mixture of 3464 grams of finely divided ammonium nitrate and 178 grams of finely divided lead dioxide (PbO₂), prepared by dry-blending the two materials together, were added to 713 grams of the copolymer mixture in increments substantially as in Example I and mixed under the vacuum lid, but with no vacuum. After a 3 minute waiting period, 9.4 grams of Butyl-Eight were added and the mixture mixed for 15 minutes under the compression ram at a pressure of 40 p.s.i. Mixing was then continued for an additional 15 minutes, 10 of which were under atmospheric pressure and 5 of which were under a vacuum of 28 inches of mercury. The final temperature of the mixture was 150° F. and the incorporation of the oxidant and binder was satisfactory. The overall time for the run was 55 minutes, while the time required for the addition of the oxidant was 12 minutes.

The results of the above examples illustrate the advantages obtained by practicing the procedure of this invention. A savings of both time and materials is a surprising and unexpected result and a uniform product is assured.

Variations and modifications are possible within the scope of the present invention, the essence of which is the discovery that the preparation of solid propellants comprising a solid oxidant and a rubbery binder can be accomplished more easily and in a shorter time by dry-blending the solid oxidant and the burning rate catalyst before the incorporation of the oxidant into the binder composition.

That which is claimed is:

1. An improved method for producing a solid propellant composition which comprises blending from 7 to 200 parts by weight of a substantially dry solid, inorganic, strong, oxidizing salt having an average particle size of less than 200 microns with one part by weight of a substantially dry burning rate catalyst selected from the group consisting of complex cyanides of iron, ammonium dichromate, potassium dichromate, ferric oxide, and lead dioxide having an average particle size of less than 40 microns; and intimately admixing from 1 to 9 parts by weight of the resulting oxidant-catalyst blend with one part by weight of a rubbery binder composition com-

prising a copolymer prepared from a monomeric mixture comprising 50 to 95 parts by weight of a conjugated diene containing 4 to 8 carbon atoms per molecule, 5 to 50 parts by weight of a



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, admixed with 0 to 35 parts by weight of carbon black per 100 parts of copolymer.

2. The method of claim 1 wherein the oxidant is ammonium nitrate, the catalyst is milori blue, the conjugated diene is butadiene and the heterocyclic nitrogen base is 2-methyl-5-vinylpyridine.

3. The method of claim 1 wherein the oxidant is ammonium nitrate, the catalyst is ammonium dichromate, the conjugated diene is butadiene and the heterocyclic nitrogen base is 2-vinylpyridine.

4. The method of claim 1 wherein the oxidant is a mixture of ammonium nitrate and ammonium perchlorate, the catalyst is ammonium dichromate, the conjugated diene is butadiene, and the heterocyclic nitrogen base is quinoline.

5. The method of claim 1 wherein the oxidant is ammonium nitrate, the catalyst is lead dioxide, the conjugated diene is butadiene; and the heterocyclic nitrogen base is a vinyl substituted pyridine.

6. In the preparation of a solid propellant comprising from 50 to 90 weight percent of a solid, inorganic, strong, oxidizing salt from 0.5 to 14 weight percent, based upon the oxidizing salt, of a combustion catalyst and a rubbery binder material comprising 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, the improvement which comprises admixing said oxidizing salt and said catalyst; and subsequently incorporating the resulting mixture into the binder.

7. In the preparation of a solid propellant comprising from about 7 to about 200 parts by weight of a substantially dry, solid, inorganic, strong, oxidizing salt having an average particle size of less than 200 microns, about 1 part by weight of a substantially dry burning rate catalyst selected from the group consisting of complex cyanides of iron, ammonium dichromate, potassium dichromate, ferric oxide, and lead dioxide having an average particle size of less than 40 microns, and from about 1 to about 9 parts by weight of the resulting oxidizing salt-catalyst blend for each part by weight of a rubbery binder composition comprising a copolymer prepared from a monomeric mixture comprising 50 to 95 parts by weight of a conjugated diene containing 4 to 8 carbon atoms per molecule, 5 to 50 parts by weight of a



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, admixed with 0 to 95 parts by weight of carbon black per 100 parts of copolymer, and from 0.75 to 20 parts by weight per 100 parts of copolymer of compounding agents selected from the group consisting of vulcanizing agents, quarternizing agents, vulcanizing accelerators, softeners, stabilizers, and surface active agents, the improvement which comprises admixing said oxidizing salt and said catalyst; and subsequently incorporating the resulting mixture into the rubbery binder composition.

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