United States Patent Office 3,053,709 Patented Sept. 11, 1962

3,053,709

COOLING SOLID PROPELLANT COMPOSITIONS DURING MIXING

Charles H. Herty III, Waco, Tex., assignor to Phillips Petroleum Company, a corporation of Delaware

No Drawing. Filed Sept. 8, 1959, Ser. No. 838,795
9 Claims. (Cl. 149—19)

This invention relates to improved, solid propellant compositions and to a method for their preparation. In one aspect the invention relates to producing a solid, rubber-base propellant having a higher burning rate and a higher extrusion rate than prior art propellant compositions. This invention also relates to a method for cooling solid propellant compositions during mixing by adding thereto Dry Ice. In still another aspect this invention relates to a method for reducing the pre-curing or scorching of the rubber binder of a propellant composition during the manufacture of the propellant.

Recently it has been discovered that superior solid propellant compositions are obtained comprising an inorganic oxidizing salt such as ammonium nitrate or ammonium perchlorate, and a rubber material such as natural rubber or synthetic rubber which act as a fuel and as a binder in the propellant composition. One example of synthetic rubber is a copolymer of butadiene and a vinylpyridine or other substituted heterocyclic nitrogen base compound which, after incorporation therein of the solid, inorganic oxidizing salt, 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, now U.S. Patent No. 3,003,861, issued October 10, 1961.

Various materials have been added to such propellant compositions to increase their burning rates. Such materials are commonly called burning rate catalysts. Ammonium dichromate and/or milori blue are materials which have been suggested as burning rate catalysts for such propellants.

In the preparation of solid propellant compositions comprising a solid inorganic oxidizing salt and a rubbery binder, the solid, inorganic salt is incorporated into the uncured rubbery binder material so that the binder forms the continuous phase and the solid inorganic salt is present as a discontinuous phase. In order to incorporate a large amount of solid, inorganic oxidizing salt into a relatively small amount of binder material it is necessary that a great deal of work be expended upon the mixture with the result that a large amount of heat is generated which must be dissipated so as to avoid raising the temperature of the mixture to a point at which pre-curing of the binder material results or to a temperature at which decomposition of the inorganic oxidizing salt might result. It is the usual practice of the prior art to utilize indirect heat exchange by means of a jacketed mixer to remove the heat generated in mixing the ingredients of the propellant composition and also to stop the mixing operation at intervals to allow the mixture to cool during the mixing operation. Some of the large mixers applicable for mixing propellant compositions are not equipped for indirect heat exchange and frequent shutdowns are required during the mixing operation to avoid overheating the ingredients of the propellant compositions being prepared.

It is an object of this invention to provide an improved method for cooling the ingredients of a solid propellant composition during the manufacture thereof. It is also an object of this invention to provide a method for cooling the ingredients of a solid propellant composition during the mixing thereof by direct heat exchange. The provision of a propellant composition wherein the rubber binder has not been subjected to pre-curing conditions is still another object of this invention. A further object of this invention is the provision of a propellant composition having improved burning rate and extrusion characteristics. Other and further objects and advantages of this invention will appear to one skilled in the art upon study of this disclosure including the detailed description of the invention.

Broadly, the invention contemplates cooling the ingredients of a solid propellant composition during the mixing together of those ingredients by adding solidified carbon dioxide, usually referred to as Dry Ice, to the mixture. The Dry Ice can be added intermittently as required to prevent overheating the propellant mix or can be added continuously so as to maintain the temperature range of the propellant mix within predetermined limits during the mixing operation. The addition of Dry Ice during incorporation of the solid oxidizer into the binder material eliminates the necessity for indirect heat exchange and makes possible the use of large-size mixing apparatus wherein no provision is made for indirect heat exchange. Cooling the propellant mix during incorporation of the oxidizer into the binder eliminates the necessity for periodically stopping the mixing operation to allow the propellant mix to cool.

The invention is not limited to the use of a solid propellant containing ammonium nitrate or ammonium perchlorate and a rubbery binder such as that previously described, but is applicable to any solid propellant wherein a solid oxidizer is incorporated into a binder material wherein the incorporating operation requires expending work upon the mix so that heat which is generated must be dissipated in some manner. Thus, a solid propellant containing ammonium nitrate or ammonium perchlorate and a rubbery binder comprising natural rubber or any of the synthetic rubbers is also applicable. Other solid propellant compositions include ammonium nitrate and an asphalt binder and ammonium nitrate or ammonium perchlorate and various binder materials such as thiokol polysulfide rubber, polyvinyl chloride, polybutadiene, and so forth, and nitroguanidine, sodium nitrate or potassium nitrate with suitable binder materials such as those set forth above.

A novel solid propellant which is applicable in the practice of the method of this invention is one comprising ammonium nitrate oxidizer, conjugated diene-heterocyclic nitrogen base copolymer, and a high energy material such as aluminum, lithium, magnesium, or hydrides such as lithium aluminum hydride ($LiAlH_4$), lithium hydride (LiH), magnesium hydride (MgH_2), etc.

The rubbery materials which are applicable for use as the binder and fuel components of the solid propellant compositions include natural and synthetic rubbery polymers which commonly are characterized by Mooney values (ML–4) in the range of about 10 to about 75. The types of rubbery materials which are useful include: natural rubber and synthetic rubber such as polysulfide rubber, silicone rubber, polybutadiene, butadiene-styrene copolymers, butadiene-acrylonitrile copolymers, and copolymers of butadiene with a copolymerizable heterocyclic base of the pyridine and quinoline series containing a $CH_2{=}C<$ group such as 2-methyl-5-vinylpyridine. Commonly preferred rubber binders are copolymers prepared by copolymerization of a major amount of a conjugated diene such as 1,3-butadiene with a minor amount of a copolymerizable monomer containing the $CH_2{=}C<$ group such as 2-methyl-5-vinylpyridine. The 90/10 copolymer of 1,3-butadiene/2-methyl-5-vinylpyridine has been found to be particularly suitable and is frequently preferred because of the favorable physical characteristics

of the resulting propellant composition when such copolymer is used as the binder component.

These rubber polymers are compounded, as is well known in the rubber art, with a reinforcing filler such as carbon black, with antioxidants, with plasticizers, and with curing agents such as vulcanizing or quaternizing agents.

The plasticizers include the known rubber plasticizers such as compounds including dioctyl phthalate, benzophenone, amylbiphenyl, di(butoxyethoxyethoxy)methane, trioctyl phosphate, tricresol phosphate, and liquid polymers of 1,3-butadiene. These plasticizers are commonly used in amounts of 0 to about 25 parts by weight per 100 parts by weight of rubber. The plasticizer is generally used in amounts sufficient to soften the rubber so as to facilitate incorporation of the oxidizer therein.

Curing agents for use with rubbery copolymers are well known in the art and include sulfur, sulfur-liberating materials, such as thiuram disulfides, polysulfides, alkylphenol sulfides and N,N'-dithioamines. Nonsulfur curvatives are also known. Accelerator-activators are frequently used in conjunction with the curing agents and examples of such compounds include lead oxide, zinc oxide, magnesium oxide, mixtures of magnesium oxide and carbon, lead carbonate, hydrated lime, lead silicate, dibutyl ammonium oleate, oleic acid, dibenzylamine, linseed oil, fatty acids, rosin acids, triethanolamine, zinc stearate, and the like. When the copolymers include a heterocyclic nitrogen base, as hereinbefore described, as one of the monomers, quaternizing agents are sometimes used as the curing agent. These quaternizing agents include various alkyl halides such as methyl iodide, ethyl iodide, hexyl iodide, octyl bromide; various alkylene halides such as propylene chlorides; various substituted alkanes which contain at least one hydrogen attached to the carbon atom attached to a halogen such as chloroform, 1,3-dichloropropane, ethylene chlorohydrin; various substituted aromatic compounds such as picryl chloride, benzyl chloride, benzene sulfonyl chloride, benzal chloride, benzotrichloride, methylbenzene sulfonate; and various polyhalogenated cycloalkanes such as hexachlorocyclopentadiene, and hexachloro-p-xylene.

Antioxidants commonly used in rubber compounding can be employed and these include hydroquinone, monobenzyl ether, phenyl-beta-naphthalamine, polymerized trimethyldihydroquinoline, heptylated diphenylamine, mono esters of salicylic acid, hexachloronaphthalene, hydrocarbon waxes, etc.

The above list of rubbery polymers, plasticizers, and other compounding ingredients is illustrative but is not exhaustive of the compounds which can be employed and is not to be considered as limiting. The rubbery polymer, together with such compounding ingredients as are required or desired to obtain a specific result comprise that which is designated as the binder component of the propellant composition. In the practice of the present invention, the binder is commonly used in amounts of 5 to 15 parts by weight for correspondingly 84 to 94 parts by weight of one or more solid oxidizers and about one part of burning rate catalyst per 100 parts by weight of propellant.

A general formulation for a binder composition is given in Table I below.

TABLE I

Composition:	Parts by weight
Rubbery copolymer (as hereinbefore described)	100
Reinforcing agent	0–100
Plasticizer	0–25
Antioxidant	0–3
Sulfur	0–2
Accelerator-activator	0–5
Alkyl halide	0–5

Suitable oxidizers include solid, inorganic oxidizing salts

such as one or more of the ammonium and alkali metal salts of nitric and perchloric acids including ammonium nitrate, potassium nitrate, sodium nitrate, lithium nitrate, ammonium perchlorate, potassium perchlorate, and the like. Phase-stabilized ammonium nitrate, which comprises about 6 to 15 percent by weight of potassium nitrate in admixture with the ammonium nitrate, is frequently a preferred oxidizer because such stabilized ammonium nitrate is less sensitive to temperature changes. These inorganic oxidizing salts can be used with minor amounts of organic oxidizers and modifiers.

Burning rate catalysts include finely divided iron oxide, ammonium dichromate, milori blue (prepared in the presence of naphthenic acid), and other complex metal cyanides including the complex cyanides of iron and nickel, such as ferric ferrocyanide and ferrous ferricyanide and are used in amounts of about 0.1 to about 10 percent by weight of the solid propellant composition. The burning rate catalyst can be omitted if desired.

Solid, high-energy fuels, such as powdered metals including magnesium, boron, aluminum and iron, are also sometimes used in amounts up to about 10 percent by weight of the solid propellant composition.

Example

In order to present a suitable example a rubber base propellant was chosen of a representative type, with the following formulation.

TABLE II

Ingredients	Parts by Weight	Percent by Weight
Bd–MVP (90:10) Copolymer [1]	10.31	9.69
Philblack A [2]	2.32	2.18
ZP–211 [3]	2.06	1.94
Flexamine [4]	0.31	0.29
Milori Blue [5]	2.00	1.88
Ammonium Dichromate	4.00	3.75
Ammonium Nitrate [6]	85.00	79.80
Magnesium Oxide	0.50	0.47
Total Parts or Percent	106.50	100.00

[1] A rubber copolymer of 90 parts butadiene and 10 parts methylvinylpyridine by weight.
[2] A carbon black of the furnace black type.
[3] 5,8,11,13,16,19-hexoxa-n-tricosane.
[4] A physical mixture of 65 percent by weight of a complex diarylamine-ketone reaction product and 35 percent of N-N'-diphenyl-p-phenylenediamide.
[5] A pigment similar to Prussian blue but having a red tint and prepared by the oxidation of a paste of potassium ferrocyanide and ferrous sulfate
[6] Contained 10 weight percent potassium nitrate.

The propellant composition was prepared according to Table II above and was mixed in two separate batches (A) and (B) in the following manner. Both batches (A) and (B) contained identical ingredients and were given the same amount of mixing time and the same treatment up to a point after the last addition of the dry salts in Table II. As is common practice in the preparation of propellant compositions, all of the ingredients except the ammonium nitrate were mixed together in a 0.7 gallon Baker-Perkins mixer and the ammonium nitrate was then added in five equal portions, mixing two minutes between additions. Batch (A) was mixed for five minutes after the final addition of ammonium nitrate and then 10 weight percent of crushed Dry Ice, based on total propellant mix, was added after which mixing was continued for another seven minutes and an additional 10 weight percent of Dry Ice was added followed by five more minutes of mixing, making a total of 17 minutes of continuous mixing with two additions of Dry Ice. The mixer was then evacuated and mixing continued for three minutes at which time sample No. 1 was taken and another 10 weight percent of Dry Ice was added and mixing continued for eight minutes at which time sample No. 2 was taken.

Batch (B) was mixed continuously for 17 minutes after the last addition of ammonium nitrate, using indirect heat exchange with cooling water to control the tem-

perature of the propellant mix after which the mixer was evacuated and mixing continued for three minutes at which time sample No. 3 was taken. Mixing was continued for eight more minutes under vacuum and sample No. 4 was taken.

TABLE III

STRAND DATA

Sample No.	Extrusion Rate @ 1,500 p.s.i.	Burning Rate @ 600 p.s.i.
	In./min.	*In./sec.*
1	135	0.229
2	164	0.241
3	112	0.209
4	74.5	0.223

The above data show that cooling the mix with Dry Ice resulted in a propellant composition having higher extrusion rates and higher burning rates. The temperature of mix (B) attained a maximum of 98° F. whereas the temperature of the mix of batch (A) attained a maximum of 85° F. during the mixing operations. Continuous mixing with indirect cooling was possible because of the small size of the mixer used; however, periodic shutdowns are required for cooling when commercial sized mixers are utilized if cooling is by indirect heat exchange. Thus, this invention provides an additional benefit, that being elimination of shutdown periods for cooling during the mixing of propellant compositions.

The mixing of the propellant ingredients may be done in any commercial chemical mixing machine, generally power driven. The actual mixing machine employed in the specific example was a Baker-Perkins 0.7 gallon working capacity Model 4–AN2 with sigma blades of cast steel. In general this machine is very much as shown in expired patents to Pfleiderer, 254,042, February 21, 1882, and 534,968, February 26, 1895, which could have been used just as well. In the commercial exploitation of the present invention a much larger mixer such as the Model 17–NEM of 200 gallons' working capacity (used widely to make smokeless powder in World War II), or the Model 24–REM of 1200 gallons' working capacity, will be employed. The size or exact shape of the machine does not vary the process, and even the smallest of these machines can be fed Dry Ice in 4 by 8 by 1 inch blocks or even somewhat larger size blocks, down to any smaller siz, and the blades will cut the Dry Ice up fine and mix it in with the other ingredients in a very thorough and rapid manner.

The Dry Ice will be added continuously or in increments in an amount sufficient to maintain the temperature of the mix within predetermined limits. If stabilized ammonium nitrate, e.g. ammonium nitrate containing a small amount of potassium nitrate, is used the mixing temperature can encompass a relatively large range such as about 70 to about 190° F. If unstabilized or pure ammonium nitrate is used the temperature should be maintained above about 90° F. to insure that the ammonium nitrate is maintained in the phase which occupies the greatest volume, i.e. phase III. Thus pure ammonium nitrate should be processed in a temperature range of about 90 to about 190° F. whereas oxidizers which are not subject to a phase change can be processed in the range of about 70 to about 190° F.

Reasonable variations and modifications are possible within the scope of this disclosure without departing from the spirit and scope of the invention.

That which is claimed is:

1. An improved method for preparing an extrudable solid propellant composition comprising an inorganic oxidizing salt and an organic binder therefore which comprises admixing said salt and said binder to incorporate said salt into said binder; and adding Dry Ice to said mixture during said mixing step to maintain the temperature of the mixture below a predetermined value.

2. In the proces of manufacturing an extrudable solid propellant composition comprising an inorganic oxidizing salt and a rubber binder wherein the inorganic oxidizing salt is incorporated into the rubber binder so that the rubber binder forms the continuous phase and the solid inorganic salt forms a discontinuous phase, the improvement comprising adding Dry Ice to the mixture of rubber and salt during the step of incorporating the salt into the rubber in an amount sufficient to maintain the temperature of the mixture within a predetermined range.

3. The process of claim 2 wherein the temperature is maintained between about 70 and about 190° F.

4. The process of claim 3 wherein the inorganic oxidizing salt is stabilized ammonium nitrate containing about 10 weight percent potassium nitrate.

5. The process of claim 3 wherein the inorganic oxidizing salt is ammonium perchlorate.

6. The process of claim 2 wherein the inorganic oxidizing salt is substantially pure ammonium nitrate and the temperature is maintained between about 90 and about 190° F.

7. The process of claim 1 wherein the organic binder is rubber.

8. The process of claim 1 wherein the organic binder is asphalt.

9. In the process of manufacturing a solid propellant composition comprising an inorganic oxidizing salt and a rubber binder wherein the inorganic oxidizing salt is incorporated into the uncured rubber binder after which the mixture is extruded and cured, the improvement comprising adding Dry Ice to the mixture of inorganic oxidizing salt and uncured rubber during the step of incorporating the inorganic oxidizing salt into the rubber in an amount sufficient to maintain the mixture at a temperature below the precuring temperature of the rubber binder.

References Cited in the file of this patent

UNITED STATES PATENTS

2,900,242 Williams et al. ---------- Aug. 18, 1959

OTHER REFERENCES

Chem. and Eng. News, Oct. 7, 1957, pages 62–3.