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2,963,356

BURNING RATE CATALYSTS FOR AMMONIUM
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7 Claims. (Cl. 52—.5)

This invention relates to solid propellants. More particularly, this invention relates to a new class of burning rate catalysts for solid propellants.

Recently it has been discovered that superior solid propellant materials are obtained comprising a solid oxidant such as ammonium nitrate or ammonium perchlorate, and a rubbery copolymer of butadiene and a vinylpyridine or other vinyl substituted heterocyclic nitrogen base compound, which after incorporation of the oxidant 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

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An object of this invention is to provide a new class of burning rate catalysts for solid propellants prepared from ammonium nitrate and a rubbery binder. A further object of this invention is to provide such propellants having increased burning rates.

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

It is believed that this invention can be best understood from a specific example including a series of runs employing this new group of burning rate catalysts.

In the following table a series of catalyst systems are set forth and the burning rate is given at two different pressures. In each case, the amount used is given as parts by weight per 100 parts of the propellant. The column headed "temperature of reaction with N₂O" refers to the temperature at which the catalyst compound begins to react with N₂O. The tests with nitrous oxide were made with the catalyst, finely divided, in a tube which was inside a furnace. The nitrous oxide was passed through the tube at a flow rate sufficient to maintain a fairly pure atmosphere over the material. The temperature was gradually increased during each run and visual observations were made to determine when the reaction occurred. The burning rate of the propellant is about 0.100 inch per second when no burning rate catalyst is used.

TABLE I

Reaction of catalyst systems with nitrous oxide

[Strand data *r* vs. *P* curve]

Propellant	Catalyst System, Parts	<i>r</i> at 600 p.s.i. (in./sec.)	<i>r</i> at 1,000 p.s.i. (in./sec.)	<i>n</i>	Temperature of Reaction with N ₂ O, ° C.	Remarks
1	2.0 Milori blue	0.144	0.199	0.58	300	Flames, no heating of the solid phase.
2	2.0 Milori blue	0.153	0.211	0.61	340	
3	4.0 Sodium borohydride	0.147	0.204	0.64	220	
4	2.0 Milori blue	0.158	0.225	0.55	400	Vigorous glow.
5	4.0 Zirconium hydride	0.168	0.223	0.52	400	Do.
6	2.0 Milori blue	0.191	0.246	0.51	220	Do.
7	4.0 Zirconium carbide	0.165	0.201	-----	300	

25, 1952, and now abandoned, by W. B. Reynolds and J. E. Pritchard.

Various materials have been added to these compositions in order to increase the burning rate thereof. I have discovered that a group of metals, metal hydrides, or metal carbides will increase the burning rate of these propellants in which the ammonium nitrate is used as the oxidant. Metals, metal hydrides, or metal carbides which are applicable are those which react with nitrous oxide at initial temperatures below 406° C. and which do not react with ammonium nitrate at temperatures below 60° C. These materials react with the nitrous oxide to give a glowing hot solid and act as an ignition source behind the flame, thereby increasing the burning rate of the propellants. They should not react with ammonium nitrate below 60° C., in order to eliminate the possibility of reaction in storage. Examples of these compounds include sodium borohydride, zirconium, zirconium hydride, zirconium carbide, titanium and cerium. These compounds are added to the solid propellant during the formulation thereof and are preferably added as finely divided materials. Broadly, the amount of these materials added is in the range of 0.5 to 10 parts per 100 parts of total propellant, 1 to 4 parts being most commonly used.

Therefore, the following are objects of this invention:

It is readily obvious from the data in this table that there is a correlation between the reaction temperature of each material with nitrous oxide at atmosphere pressure and the burning rate increase. Those materials which have a low temperature of reaction with nitrous oxide increase the burning rate more than those with a high reaction temperature.

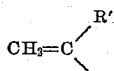
The rubbery polymers employed as binders in the solid propellant compositions of this invention are copolymers of conjugated dienes with polymerizable heterocyclic nitrogen bases of the pyridine series. These copolymers can vary in consistency from very soft rubbers, i.e., materials which are soft at room temperature but will show retraction when relaxed, to those having a Mooney value (ML-4) up to 100. Copolymers of higher Mooney value can be used if large softener loadings are used. The rubbery copolymers most frequently preferred have Mooney values in the range between 10 and 40. They may be prepared by any polymerization methods known to the art, e.g., mass or emulsion polymerization. One convenient method for preparing these copolymers is by emulsion polymerization at temperatures in the range between 0 and 140° F. Recipes such as the iron pyrophosphate-hydroperoxide, either sugar-free or containing sugar, the sulfoxylate and the persulfate recipes are among those which are applicable. It is ad-

vantageous to polymerize to high conversion as the unreacted vinylpyridine monomer is difficult to remove by stripping.

The conjugated dienes employed are those containing from 4 to 6 carbon atoms per molecule and include 1,3-butadiene, isoprene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and the like. Various alkoxy, such as methoxy and ethoxy and cyano derivatives of these conjugated dienes, are also applicable. Thus, other dienes, such as phenylbutadiene, 2,3-dimethyl-1,3-hexadiene, 2-methoxy-3-ethylbutadiene, 2-ethoxy-3-ethyl-1,3-hexadiene, 2-cyano-1,3-butadiene, are also applicable in the preparation of the polymeric binders of this invention.

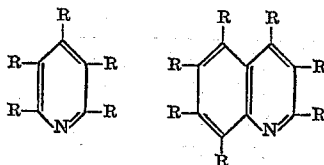
Instead of using a single conjugated diene, a mixture of conjugated dienes can be employed. Thus, a mixture of 1,3-butadiene and isoprene can be employed as the conjugated diene portion of the monomer system.

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

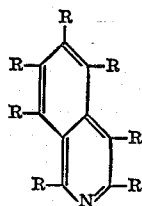


substituent wherein R' is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl (isopropenyl) group. Of these, the compounds of the pyridine series are of the greatest interest commercially at present. Various substituted derivatives are also applicable but the total number of carbon atoms in the groups attached to the carbon atoms of the heterocyclic nucleus should not be greater than 12 because the polymerization rate decreases somewhat with increasing size of the alkyl group. Compounds where the alkyl substituents are methyl and/or ethyl are available commercially.

These heterocyclic nitrogen bases have the formula



or



where R is selected from the group consisting of hydrogen, alkyl, vinyl, alpha-methylvinyl, alkoxy, halo, hydroxy, cyano, aryloxy, aryl, and combinations of these groups such as haloalkyl, alkylaryl, hydroxyaryl, and the like; one and only one of said groups being selected from the group consisting of vinyl and alpha-methylvinyl; and the total number of carbon atoms in the nuclear substituted groups, in addition to the vinyl or alpha-methylvinyl group, being not greater than 12. Examples of such compounds are 2-vinylpyridine; 2-vinyl-5-ethylpyridine; 2-methyl-5-vinylpyridine; 4-vinylpyridine; 2,3,4-trimethyl-5-vinylpyridine; 3,4,5,6-tetra-methyl-2-vinylpyridine; 3-ethyl-5-vinylpyridine; 2,6-diethyl-4-vinylpyridine; 2-isopropyl-4-nonyl-5-vinylpyridine; 2-methyl-5-undecyl-3-vinylpyridine; 2,4-dimethyl-5,6-dipentyl-3-vinylpyridine; 2-decyl-5-(alpha-methylvinyl)pyridine; 2-vinyl-3-methyl-5-ethylpyridine; 2-methoxy-4-chloro-6-vinylpyridine; 3-vinyl-5-ethoxypyridine; 2-vinyl-4,5-dichloropyridine; 2-(al-

pha-methylvinyl)-4-hydroxy-6-cyanopyridine; 2-vinyl-4-phenoxy-5-methylpyridine; 2-cyano-5-(alpha-methylvinyl)pyridine; 3-vinyl-5-phenylpyridine; 2-(para-methylphenyl)-3-vinyl-4-methylpyridine; 3-vinyl-5-(hydroxyphenyl)-pyridine; 2-vinylquinoline; 2-vinyl-4-ethylquinoline; 3-vinyl-6,7-di-n-propylquinoline; 2-methyl-4-nonyl-6-vinylquinoline; 4-(alpha-methylvinyl)-8-dodecylquinoline; 3-vinylisoquinoline; 1,6-dimethyl-3-vinylisoquinoline; 2-vinyl-4-benzylquinoline; 3-vinyl-5-chloroethylquinoline; 3-vinyl-5,6-dichloroisoquinoline; 2-vinyl-6-ethoxy-7-methylquinoline; 3-vinyl-6-hydroxymethylisoquinoline; and the like. Mixtures of these heterocyclic nitrogen bases can be used, if desired.

The polymer used as the binder in the propellant runs 15 previously described was a portion of the product produced in a series of 55 runs. The following recipe was used:

	Parts by weight
20 Butadiene	90
2-methyl-5-vinylpyridine	10
Water	200
Potassium fatty acid soap	6.0
KCl	0.1
25 Sodium alkyl aryl sulfonate	0.3
Tetra sodium salt of ethylenediamine tetracetate acid	0.005
Tertiary dodecyl mercaptan	Variable
Ferrous sulfate heptahydrate	0.2
30 Potassium pyrophosphate	0.253
Paramethane hydroperoxide	0.1 or 0.135

Polymerization was conducted at 41° F. To maintain the desired Mooney, the modifier was charged in two increments, an average of 0.48 part in the initial charge and 0.20 part at 60 percent conversion. This gave an average blowdown Mooney (ML-4) of 21. The paramethane hydroperoxide was used at the 0.1 level for the first 10 runs and thereafter increased to 0.135 part. The average reaction time was 17.2 hours to 85.9 percent conversion. The short-stop used was potassium dimethyl dithiocarbamate in an amount of 0.15 part. The polymer was stabilized by adding 1.75 percent by weight based on the polymer of phenyl-beta-naphthylamine.

The latex was masterbatched with 19.5 parts of Phil-black A carbon black per 100 parts of rubber and acid coagulated. The crumb was caustic (potassium hydroxide) washed at a high pH to convert the organic acid to soap which was washed out to obtain a product with low organic acid and soap and subsequently dried.

The binder for propellants 1 through 6 was as follows:

	Parts by weight
55 Copolymer	100
Carbon black	20
ZP-211 ¹	20
Flexamine ²	3

¹ 5,8,11,13,16,19-hexoxa-n-tricosane.
² A physical mixture containing 65 percent of a complex diarylamine-ketone reaction product and 35 percent of N,N'-diphenyl-p-phenylenediamine.

The binder for propellant 7 was as follows:

	Parts by weight
Copolymer	100
Carbon black	20
70 Benzophenone	20
Flexamine ¹	3.0
N,N-dimethyl-S-tert-butylsulfenyl dithiocarbamate	1.0
Sulfur	0.75
Zinc oxide	3.0

¹ 5,8,11,13,16,19-hexoxa-n-tricosane.

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The complete composition of each propellant is shown in the following table:

	1	2	3	4	5	6	7
Binder.....	16.5	16.5	16.5	16.5	16.5	16.5	17.5
Ammonium Nitrate.....	83.5	83.5	83.5	83.5	83.5	83.5	82.5
MgO.....	0.5	0.5	0.5	0.5	0.5	0.5	---
Milori Blue.....	2.0	2.0	2.0	2.0	4.0	2.0	4.0
Sodium Borohydride.....	---	4	---	---	---	---	---
Zirconium Metal Powder.....	---	---	4	---	---	4	---
Zirconium Hydride.....	---	---	---	4	---	---	---
Zirconium Carbide.....	---	---	---	---	4	---	---

For each run, the polymer was placed on a roll mill and additional black was added to bring the loading to the desired level. The Flexamine was also added on the mill. The resulting mixture was placed in a Baker-Perkins mixer and the plasticizer and magnesium oxide and curatives, if used, were added and the composition mixed until a homogeneous mixture was obtained. The catalyst and ammonium nitrate were blended together and added to the binder in four portions, each time the mixing being continued until the mixer started drawing power. A final mixing of 5 to 10 minutes after addition of all the oxidizer was provided to insure uniformity.

The propellant was made into strands by extruding it under a pressure of 8000 p.s.i.

Regular propellant grade ammonium nitrate or ammonium perchlorate is used as the oxidant in the propellants of my invention. It should be finely divided, preferably in a range of 300 to 10 microns average particle size. The amount of oxidant is generally in the range of 50 to 90 percent by weight of the total of the oxidant and binder. If desired, however, less than 50 percent by weight can be used.

The combustion rate catalysts of my invention can be used alone or in combination with combustion rate catalysts known in the art, such as ammonium dichromate and metal ferrocyanides and ferricyanides. Ferric ferrocyanides, such as Prussian, Berlin, Hamburg, Chinese, Paris and Milori blue, soluble ferric ferrocyanide, such as soluble Berlin or Prussian blue which contains potassium ferric ferrocyanide, and ferric ferrocyanide which has been treated with ammonia, are among the materials which can be used. Ferrous ferricyanide, Turnbull's blue is also applicable. Milori blue is a pigment similar to Prussian blue but having a red tint and is prepared by the oxidation of a paste of potassium ferrocyanide and ferrous sulfate. Other metal compounds such as nickel and copper ferrocyanides can also be employed.

The amount of burning rate catalyst used, in the propellant compositions of this invention, are usually in the range of 1 to 60 parts per 100 parts of rubbery polymer with from 5 to 50 parts being most frequently preferred. The amount of combustion catalyst will usually be 0.5 to 10 parts by weight per hundred parts of oxidant and binder, with a range of 1 to 4 parts being preferred. When the combination catalysts are used from 0.5 to 10 parts of the catalyst according to the present invention (metal, metal carbide, or metal hydride) is used per 100 parts by weight of propellant and from 0.25 to 5 parts of the prior art catalyst such as Milori blue are used.

The binder contains a rubbery copolymer of the type hereinbefore described and, in addition, there can be present one or more reinforcing agents, plasticizers, wetting agents, and antioxidants. Other ingredients which are employed for sulfur vulcanization include a vulcanization accelerator, a vulcanizing agent such as sulfur, and an accelerator activator, such as zinc oxide.

The copolymer comprising a conjugated diene and a polymerizable heterocyclic nitrogen base can also be cured by a quaternization reaction by incorporating therein a quaternizing agent and subjecting the resulting mixture to quaternizing conditions of temperature. Suitable quaternizing agents include alkyl halides such as methyl iodide, methyl bromide; alkylene halides such as

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methylene iodide, ethylene bromide; substituted alkanes such as chloroform, bromoform; alkyl sulfates such as methyl sulfate; and various substituted aromatic compounds such as benzoyl chloride, methyl benzene sulfonate, and the like.

The quaternizing temperature is usually in the range zero to 175° C., although temperatures outside this range can be used.

A general formulation for a binder composition prepared by sulfur vulcanization is given below:

	Parts by weight
Rubbery copolymer (as hereinbefore described) ..	100
Reinforcing agent	0-50
Plasticizer	0-100
15 Wetting agent	0-10
Antioxidant	0-3
Vulcanization accelerator	0-5
Sulfur	0-2
20 Zinc oxide	0-5

Reinforcing agents include carbon black, silica gel, lignin, and various reinforcing resins such as styrene-divinylbenzene, methyl acrylate-divinylbenzene, acrylic acid-styrene-divinylbenzene, and methyl acrylate-acrylic acid-divinylbenzene resins.

In general, any rubber plasticizers can be employed in these binder compositions. Materials such as Pentaryl A (amylbiphenyl), Paraflux (saturated polymerized hydrocarbon), Circosol-2XH (petroleum hydrocarbon softener having a specific gravity of 0.940 and a Saybolt Universal viscosity at 100° F. of about 2000 seconds), di (1,4,7-trioxaundecyl)methane, and dioctyl phthalate are suitable plasticizers. Materials which provide rubber having good low temperature properties are preferred. It is also frequently preferred that the plasticizers be oxygen-containing materials.

Wetting agents aid in deflocculating or dispersing the oxidizer, Aerosol OT (dioctyl ester of sodium sulfosuccinic acid), lecithin, and Duomeen C diacetate (the diacetate of trimethylene diamine substituted by a coconut oil product) are among the materials which are applicable.

Antioxidants include Flexamine (physical mixture containing 65 percent of a complex diarylamine-ketone reaction product and 35 percent of N,N'-diphenyl-p-phenylenediamine), phenyl-beta-naphthylamine, 2,2-methylenebis(4-methyl-6-tert-butylphenol), and the like. Rubber antioxidants, in general, may be employed or if desired may be omitted.

Examples of vulcanization accelerators are those of the carbamate type, such as N,N-dimethyl-S-tert-butylsulfenyl dithiocarbamate and Butyl-Eight. Butyl Eight is a rubber accelerator of the dithiocarbamate type described in "Handbook of Material Trade Names" by Zimmerman and Lavine, 1953 edition, as a brown liquid; specific gravity 1.01; partially soluble in water and gasoline; and soluble in acetone, alcohol, benzol, carbon disulfide and chloroform.

It is to be understood that each of the various types of compounding ingredients may be used singly or mixtures of various ingredients performing a certain function may be employed. It is sometimes preferred, for example, to use mixtures of plasticizers rather than a single material.

The various ingredients in the propellant composition may be mixed on a roll mill or an internal mixer such as a Banbury or a Baker-Perkins dispersion blade mixer may be employed. The binder forms a continuous phase in the propellant with the oxidant as the discontinuous phase.

Rocket grains are formed by compression molding, injection molding, or extrusion.

The curing temperature will be limited by the oxidizer employed in some cases but will generally be in the range between 70 and 250° F., preferably between 170 and 200° F.

The curing time must be long enough to give required creep resistance and other mechanical properties in the propellant. The time will generally range from around

three hours when the higher curing temperatures are employed to seven days when curing is effected at lower temperatures.

As many possible embodiments may be made of this invention without departing from the scope thereof, it is to be understood that all matter herein set forth is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. A propellant composition comprising from 50 to 90 parts by weight of ammonium nitrate; from 10 to 50 parts by weight of a copolymer of butadiene and 2-methyl-5-vinylpyridine to make a total of 100 parts by weight; from 0.25 to 5 parts by weight of Milori blue; and from 0.5 to 10 parts by weight of sodium borohydride.

2. A propellant composition comprising from 50 to 90 parts by weight of ammonium nitrate; from 10 to 50 parts by weight of a copolymer of butadiene and 2-methyl-5-vinylpyridine to make a total of 100 parts by weight; from 0.25 to 5 parts by weight of Milori blue; and from 0.5 to 10 parts by weight of zirconium.

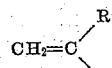
3. A propellant composition comprising from 50 to 90 parts by weight of ammonium nitrate; from 10 to 50 parts by weight of a copolymer of butadiene and 2-methyl-5-vinylpyridine to make a total of 100 parts by weight; from 0.25 to 5 parts by weight of Milori blue; and from 0.5 to 10 parts by weight of zirconium hydride.

4. A propellant composition comprising from 50 to 90 parts by weight of ammonium nitrate; from 10 to 50 parts by weight of a copolymer of butadiene and 2-methyl-5-vinylpyridine to make a total of 100 parts by weight; from 0.25 to 5 parts by weight of Milori blue; and from 0.5 to 10 parts by weight of zirconium carbide.

5. A propellant composition comprising from 50 to 90 parts by weight of ammonium nitrate; from 10 to 50 parts by weight of a copolymer of butadiene and 2-methyl-5-vinylpyridine to make a total of 100 parts by weight; from 0.25 to 5 parts of 100 parts by weight; from 0.25

to 5 parts by weight of Milori blue; and from 0.5 to 10 parts by weight of titanium.

6. A propellant composition comprising from 50 to 90 parts by weight of ammonium nitrate; from 10 to 50 parts by weight of a copolymer of a conjugated diene having up to 8 carbon atoms per molecule with at least one



10 substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl substituted pyridine, and alkyl substituted quinoline, wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 12 and wherein R' is selected from the group consisting of hydrogen and a methyl radical, to make a total of 100 parts by weight; from 0.25 to 15 5 parts by weight of a compound selected from the group consisting of ammonium dichromate, ferric ferrocyanide, ferrous ferricyanide, copper ferrocyanide and nickel ferrocyanide; and from 0.5 to 10 parts by weight of a material selected from the group consisting of sodium borohydride, zirconium, zirconium hydride, zirconium carbide, titanium and cerium.

20 25 7. The propellant of claim 6 wherein said copolymer is a copolymer of butadiene and 2-methyl-5-vinylpyridine.

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