

[54] COMPOSITE PROPELLANT INCLUDING
(U) POLYFUNCTIONAL AMINE

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149/76

[51] Int. Cl. C06d 5/06

[58] Field of Search 149/19, 76, 36, 60

[56] References Cited

UNITED STATES PATENTS

3,305,523 2/1967 Burnside 149/19 X

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3,476,622	11/1969	Harada et al.	149/19
3,586,552	6/1971	Potts et al.	149/19

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[57]

ABSTRACT

Propellant compositions are provided in which dewetting of the propellant composition under applied stress is substantially reduced. Reduced dewetting is achieved through the use of polyfunctional amines which are capable of forming a chemical bond between the oxidizer (oxygen containing ammonium salt) and the binder in the cured propellant.

11 Claims, No Drawings

COMPOSITE PROPELLANT INCLUDING (U) POLYFUNCTIONAL AMINE

This invention relates to novel composite propellant compositions having superior load bearing properties, stability, and mechanical properties. The propellant of this invention comprises in the form of a cured admixture a crosslinkable binder prepolymer, a crosslinking agent, an oxygen containing ammonium salt and a polyfunctional amine which contains at least one amine group more basic than ammonia and at least one amine group which is reactive with the polymeric binder. More particularly, this invention relates to composite propellant compositions in which dewetting of the propellant composition is substantially reduced through the incorporation of certain polyfunctional amines in controlled amounts, said polyfunctional amines capable of providing a primary chemical bond between the surface of the oxygen containing ammonium salt and propellant binder in the cured propellant.

Composite solid propellants are comprised of oxidizers and fuels in the form of small solid particles, sometimes referred to hereinafter as fillers, uniformly distributed in a polymeric binder. The polymeric binder functions to hold and uniformly distribute the filler particles throughout the binder.

Mechanical and ballistic properties of propellants are of primary importance in the selection of a propellant for any particular use. Mechanical and ballistic properties are known to depend on the nature of the interface between the solid filler particles and the polymeric binder. It has been discovered by various researchers in the field of solid propellants that mechanical failure of solid propellants resulting from environmental and operating stresses usually occurs at or about the binder-filler interface within the cured propellant matrix rather than in the propellant binder. Failure of composite propellant at the binder-filler interface is referred to as "dewetting".

Studies by Oberth and Bruenner reported in CPIA Publication No. 94C, Vol. II, dated October 1965, show that subscale motors containing propellants that fail in the binder phase of the propellant have markedly improved recycle properties compared to substantially identical propellants that dewet at the binder-filler interface under similar stress conditions. Still other studies have shown that composite propellants that fail under conditions of high stress exclusively in the binder phase rather than at the binder-filler interface exhibit markedly improved load bearing capability and, in general, are physically more stable propellants. Failure of propellants in the binder phase rather than at the binder-filler interface was achieved employing various additives which function to bond the ammonium perchlorate oxidizer to the propellant binder.

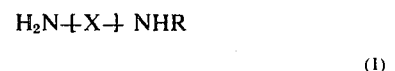
In some of the studies conducted by Oberth and Bruenner, triethanolamine was employed in an attempt to eliminate dewetting. While improved mechanical properties were achieved in a polyurethane binder employing triethanolamine as an additive, evolution of ammonia gas from these propellants caused difficulties in curing and in reproducibility of mechanical properties and resulted in porous propellant. Another additive employed in an attempt to reduce binder-filler dewetting was dihydroxypropyl-bis-2-cyanoethylamine. This material was considered superior to triethanolamine for use in polyurethane type composite propellants be-

cause ammonia was not liberated as reaction product during mixing and cure of the composition. Recent studies by C. O. Parker and T. E. Stevens reported in Redstone Research Laboratories Technical Report S-205 of January 1969 show that use of dihydroxypropyl-bis-2-cyanoethylamine increases the mix viscosity of composite propellant and complicates propellant processing.

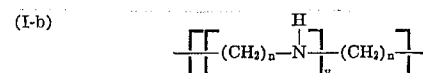
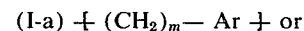
Broadly, in accordance with this invention, composite propellant compositions are provided in which the tendency of the propellant to dewet under conditions of stress is substantially reduced, said propellant compositions comprising in the form of a cured admixture a crosslinkable binder prepolymer, a crosslinking agent, an oxygen containing ammonium salt selected from the group consisting of ammonium perchlorate, ammonium nitrate, hydrazine perchlorate and hydrazine diperchlorate, and a polyfunctional amine having at least one amine group more basic than ammonia and at least one amine group reactive with and available for reaction with the polymeric binder after ammonia has been displaced from the surface of the oxygen-containing ammonium salt. The composite propellant compositions of this invention comprise by weight in the form of a cured admixture from about 60 to about 90 percent of oxygen-containing ammonium salt, from about 5 to about 20 percent of a crosslinkable binder prepolymer and crosslinking agent and from about 0.005 to about 0.05 percent of a polyfunctional amine. These compositions can optionally contain a metal or metal hydride fuel in amounts of from 0 to about 20 percent by weight.

The polyfunctional amines which can be employed in this invention include amines having one or more aliphatic amine groups which are more strongly basic than ammonia and at least one primary aromatic amine group which is less basic than ammonia; and polyfunctional aliphatic amines containing primary and secondary amine groups in which all of the amine groups are more basic than ammonia, but for steric or electronic reasons at least one of the secondary aliphatic amine groups remains free, i.e., it will not displace ammonia from the surface of ammonium perchlorate. The free amine group(s) of this latter class of amines are available to react with polymeric binder.

Illustrative polyfunctional amines defined above have the following structural formula:

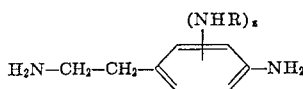


where X is either



wherein Ar is phenylene, amino-substituted phenylene, naphthylene, amino-substituted naphthylene; m is from 1 to 20, n is from 2 to 5, y is from 1 to 5 and R is hydrogen or lower alkyl having from one to four carbon atoms.

A preferred class of polyfunctional amines having the general formula I-a has the structural formula set forth below:



where z is 0, 1, 2, 3 or 4.

Illustrative polyfunctional amines which can be employed in the compositions of this invention wherein X of the general formula I is group (I-a) defined above include β -(4-aminophenyl) ethylamine; β -(2,4,6-triaminophenyl) butylamine, β -(2,4-diaminophenyl) hexylamine; β -(4-aminophenyl) decylamine; β -(2,4-diaminophenyl) tetradecylamine; 2-amino-7-naphthalenethylamine; 2-amino-7-naphthalenebutylamine; 3,5-diamino-6-naphthalenedecylamine and the like. Illustrative polyfunctional amines of formula I wherein X is group (I-b) defined above include diethylenetriamine, triethylenetetramine; tetraethylenepentamine, pentaethylenhexamine, and the like. Another suitable polyfunctional amine is polyethyleneimine. This polyfunctional amine is available commercially under the trade name "Montrek-6".

Binder systems which can be employed in the propellant compositions of this invention include all binder systems which are reactive with the polyfunctional amines described herein. These binders include those derived from polyester prepolymers such as polyesters having terminal carboxy groups and which are linear condensation products of polyhydric alcohols and polybasic acids such as set forth in U.S. Pat. No. 3,155,552; polyurethane binders prepared by reaction of a compound having two or more hydroxyl or thiol groups with an organic compound having two or more isocyanate or isothiocyanate groups such as disclosed in U.S. Pat. No. 3,296,043; and polymeric binders derived from carboxy-terminated prepolymers fully described hereinafter. The number of functional groups on at least a portion of the binder prepolymer and/or crosslinking agent must be greater than 2 so that a crosslinked propellant composition results.

Illustrative binder prepolymers and crosslinkings agents which will react with the polyfunctional amines hereinabove defined to produce the propellant compositions of this invention are set forth in Table I which follows.

TABLE I

Binder prepolymer	Prepolymer functional group reacting in the curing reaction	Curing agent functional group reacting in the curing reaction
1..... Carboxyl-terminated polybutadiene (CTPB).	Carboxyl.....	Epoxide, imine.
2..... Hydrogenated CTPB.	do.....	Do.
3..... Carboxyl-terminated polyisobutylene.	do.....	Do.
4..... Carboxyl-terminated polyacrylate esters (hydrocarbon backbone).	do.....	Do.
5..... Ethyl acrylate-acrylic acid copolymer (hydrocarbon backbone).	do.....	Do.
6..... Carboxyl-terminated polyester (polyester backbone) as in U.S. 3,155,552, col. 1, lines 54 to col. 2, line 9.	do.....	Do.
7..... Nitroso rubber.	do.....	Do.
8..... Hydroxy-terminated polybutadiene (HTPB).	Hydroxyl.....	Isocyanate, isothiocyanate.
9..... Hydrogenated (HTPB).	do.....	Do.
10..... Hydroxyl-terminated polyisobutylene.	do.....	Do.
11..... Hydroxyl-terminated polyacrylate ester.	do.....	Do.

TABLE I—Continued

Binder prepolymer	Prepolymer functional group reacting in the curing reaction	Curing agent functional group reacting in the curing reaction
12..... Ethyl acrylate-hydroxyethyl acrylate copolymer (hydrocarbon backbone).	do.....	Do.
13..... Hydroxyl-terminated fluorocarbon.	do.....	Do.
14..... Hydroxyl-terminated polyester (polyester backbone) as in U.S. 3,296,043, col. 10, lines 62-75; col. 11, lines 1-30.	do.....	Do.
15..... Low molecular weight diols (U.S. 3,296,043, col. 10, lines 7-61).	do.....	Do.
16..... Hydroxyl-terminated polyether.	do.....	Do.
17..... Hydroxyl-terminated polysulfide (as in U.S. 3,296,043, col. 11, lines 33-37).	do.....	Do.
18..... Nitrocellulose.	do.....	Do.
19..... Isocyanate-terminated polyester (polyester backbone).	Isocyanate.....	Hydroxyl. ¹

¹ As in U.S. 3,296,043, col. 12, lines 11-24.

Binder prepolymers 1-7 in Table I cure principally via the epoxide-carboxyl reaction. Binder prepolymers 8-18 cure via formation of urethane linkages from the interaction of hydroxyl and isocyanate groups. Binder prepolymer 19 cures via an isocyanate hydroxyl reaction.

Crosslinking agents which can be employed with the crosslinkable propellant binder prepolymer to effect crosslinking thereof and which will react with the polyfunctional amine to provide a chemical bond between the polyfunctional amine and the propellant binder when in a cured admixture include polyisocyanates, polyisothiocyanates, polyepoxides, and polyimines.

Illustrative polyisocyanates which can be employed include alkane diisocyanates, such as: ethylene diisocyanate and trimethylene diisocyanate; alkene diisocyanates such as 1-propylene-1,2-diisocyanate and 2-propylene-1,2-diisocyanate; alkylidene diisocyanates such as ethylidene diisocyanate; cycloalkylidene diisocyanates; cycloalkylidene diisocyanates; aromatic diisocyanates such as *m*-phenylene diisocyanate; 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate; aliphatic-aromatic diisocyanates such as xylene-1,4-diisocyanate, mixtures thereof and the like. Polyisothiocyanates corresponding to the polyisocyanates described hereinabove can be employed in place of a polyisocyanate crosslinking agent.

Illustrative polyimines which can be employed as cross-linking agents include the alkyleneimine tris-1,2-methyl aziridinyl phosphine oxide sold under the trade-name MAPO; tris-1,2-methyl aziridinyl phosphine sulfide; ethylene glycol-bis- β -propylene imine propionate; and terephthaloyl-bis-ethylene imine, mixtures thereof and the like.

Illustrative polyepoxides which can be employed are preferably mixtures of di and tri-epoxides fully defined hereinafter. Any of the diepoxides and triepoxide mixtures set forth herein can be employed for binder systems other than the preferred binder referred to herein after.

The preferred binder prepolymer to be employed in this invention is a carboxy-terminated prepolymer containing on the average not less than about two free carboxyl groups per polymer molecule and is preferably a homopolymer of an olefin such as isobutylene or a con-

jugated diene containing four to eight carbon atoms, such as butadiene-1,3; isoprene; octadiene-1,3 and the like; a copolymer of more than one olefin or conjugated diene such as an ethylene-propylene copolymer; a copolymer of a conjugated diene with other copolymerizable monomers which are preferably vinyl-substituted aromatic compounds such as styrene, the 1- or 2-vinyl naphthalenes and their alkyl, aryl, alkoxy, cycloalkyl, alkaryl, aralkyl, aryloxy, and dialkyl amino derivatives; or a mixture of any of the above homopolymers or copolymers.

The preferred carboxy-terminated prepolymers can be produced in known manner from the above monomers, as, for example, by carrying out the polymerization in the presence of, as initiators, organoalkali metal compounds of the formula RM_v , where R is an aliphatic, cycloaliphatic or aromatic hydrocarbon radical, M is an alkali metal such as sodium, potassium, lithium, cesium, or rubidium, and v is 2 to 4, and then replacing the alkali metal atoms on the ends of the polymer molecule with COOH groups by reacting with carbon dioxide and then hydrolyzing. Polymers containing two or more carboxyl groups per polymer molecule can be prepared by polymerizing an unsaturated carboxylic acid containing a single carbon to carbon double bond such as acrylic, methacrylic, itaconic, vinyl acetic, oleic, fumaric, maleic, and like acids with itself or with a different copolymerizable monomer such as, for example, a different unsaturated acid, an olefin or a conjugated diene, according to any of the known methods.

The carboxy-terminated prepolymers which are particularly useful in this invention are the carboxy-terminated polymers of butadiene and isobutylene, having molecular weights ranging from about 1,000 to about 20,000, and preferably from about 3,000 to about 10,000.

The curing agent which is employed in curing the preferred prepolymer of this invention is a mixture of diepoxides and triepoxides having a diepoxide:triepoxide mole ratio of from about 15:1 to 1:1, and preferably from 8:1 to 3:1. Maintenance of the ratio of the difunctional epoxides to the trifunctional epoxides within the above ranges is important to the production of propellants having a satisfactory mechanical property balance since below the ratio of 1:1 the propellant elongation is low, and above the ratio of 15:1 the propellant tensile strength is low.

Illustrative diepoxides which can be employed are the saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic diepoxides which also contain, if desired, non-interfering substituents. Preferred diepoxides are the aliphatic diepoxides containing four to 30 carbon atoms, the cycloaliphatic diepoxides containing 12 to 40 carbon atoms and the diglycidyl ethers of dihydric phenols. Typical diepoxides include butadiene dioxide; 1,2,5,6-diepoxyhexane; diglycidyl ether; diglycidyl ether of 1,3-butanediol; 1,8-bis(2,3-epoxypropoxy) octane; 1,4-bis(2,3-epoxypropoxy) cyclohexane; 1,4-bis(3,4-epoxybutoxy)-2-chlorocyclohexane; the di(epoxycyclohexanecarboxylates) of aliphatic diols exemplified by the bis(3,4-epoxycyclohexanecarboxylate) of 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol; ethylene glycol, 2,2-diethyl-1,3-propanediol; 1,6-hexanediol and 2-butene-1,4-diol; the oxyalkylene glycol epoxycyclohexanecarboxylates

exemplified by bis(2-ethylhexyl-4,5-epoxycyclohexane-1,2-dicarboxylate) of dipropylene glycol, bis(3,4-epoxy-6-methylcyclohexanecarboxylate) of diethylene glycol and bis(3,4-epoxycyclohexanecarboxylate) of triethylene glycol; the epoxycyclohexylalkyl epoxycyclohexanecarboxylates exemplified by 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate; 3,4-epoxy-1-methylcyclohexylmethyl 3,4-epoxy-1-methyl cyclohexanecarboxylate; 3,4-epoxy-2-methylcyclohexylmethyl 3,4-epoxy-2-methylcyclohexanecarboxylate; 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate; (1-chloro-3,4-epoxycyclohexan-1-yl) methyl 1-chloro-3,4-epoxycyclohexanecarboxylate; (1-bromo-3,4-epoxycyclohexan-1-yl) methyl 1-bromo-3,4-epoxycyclohexanecarboxylate and (1-chloro-2-methyl-4,5-epoxycyclohexan-1-yl) methyl 1-chloro-2-methyl-4,5-epoxycyclohexanecarboxylate; epoxycyclohexylalkyl dicarboxylates exemplified by bis(3,4-epoxycyclohexylmethyl) pimelate and oxalate and bis(3,4-epoxy-6-methylcyclohexylmethyl) maleate, succinate, sebacate and adipate; epoxycyclohexylalkyl phenylenedicarboxylates exemplified by bis(3,4-epoxycyclohexylmethyl) terephthalate and bis(3,4-epoxy-6-methylcyclohexylmethyl) terephthalate; bis(3,4-epoxy-6-methylcyclohexylmethyl) diethylene glycol ether; vinyl cyclohexene dioxide; diepoxide of dicyclohexene; dicyclopentadiene dioxide; bis(2,3-epoxycyclopentyl) ether; glycidyl 2,3-epoxycyclopentyl ether; 2,3-epoxycyclopentyl 2-methylglycidyl ether; 1,2,5,6-diepoxy-3-hexyne; 1,3-epoxypropoxy benzene; 1,4-bis(2,3-epoxypropoxy) benzene; 1,3-bis(4,5-epoxypentoxy)-5-chlorobenzene; 4,4'-bis(2,3-epoxypropoxy) diphenylether; 2,2-bis(2,3-epoxypropoxyphenyl) methane; 2,2-bis[p-(2,3-epoxypropoxy) phenyl] propane, i.e., the diglycidyl ether of bisphenol A; quinoline diepoxide and the like, as well as mixtures thereof.

Triepoxides can be employed and contain three epoxide groups per molecule and are aliphatic, cycloaliphatic or aromatic triepoxides. Preferred triepoxides are the triepoxyalkanes containing six to 25 carbon atoms; the triepoxycyclohexane carboxylates and the triglycidylethers of trihydric alcohols such as glycerol, 1,1,1-tri(hydroxymethyl) propane, 1,2,6-hexanetriol and the higher alcohols containing up to about 25 carbon atoms; and the triglycidyl ethers of trihydric phenols, such as phloroglucinol, the trihydroxydiphenyl methanes and propanes, the trihydroxyaminophenols, the trisphenols; mixtures thereof and the like. Epoxide mixtures containing the diglycidyl ethers of bisphenol A and the triepoxides of the aminophenols are particularly preferred.

For best results, both the diepoxide and the triepoxide of the mixture will be in the relatively pure state, i.e., having a purity of about 95 to 100 percent. The ratio of the epoxy groups in the epoxide mixture to the functional groups of the resin binder should be in substantially stoichiometric proportions. Although a slight excess of either is not harmful, it is preferred that a slight excess of epoxy groups over resin binder functional groups be present in the binder.

When employing carboxy-terminated prepolymer as the binder with an epoxide mixture as the crosslinking agent, the presence of a catalyst is required which promotes the carboxyl-epoxide reaction. The catalyst must also have high activity in the presence of the other pro-

pellant ingredients and must not adversely affect the desirable properties of the cured propellant, as by side reactions. Catalysts which have been found to fit all of the above requirements are chromium salts of aliphatic carboxylic acids containing two to 22 carbon atoms are preferably two to 18 carbon atoms, chromium naphthenate or vanadium naphthenate. The preferred catalysts include chromium acetate, chromium 2-ethylhexanoate, chromium neodecanoate, chromium stearate, chromium oleate, chromium naphthenate and vanadium naphthenate. The amount of catalyst necessary to promote the reaction will, of course, depend on many factors, as for example, on the particular metal salt employed, the binder materials and other propellant ingredients present, and the cure rate desired. In general, the amount of catalyst utilized will vary from a very small catalytic amount up to about 0.1 percent of the propellant composition and preferably will be from about 0.005 to about 0.03 percent by weight of the composition.

The composite propellant of this invention is prepared by intimately blending or mixing the ingredients heretofore described using conventional techniques and standard equipment. The solid propellant compositions of this invention are prepared by admixing the binder forming ingredients comprising a prepolymer and a crosslinking agent therefor and a polyfunctional organic amine as defined herein. To this admixture is added the oxygen containing ammonium salt. As is often the case in preparing composite propellants, the oxygen containing ammonium salt may be added in more than one particle size in order to effectively control the cured propellant burning rate. When employing oxidizer having more than one particle size range it is generally preferable to admix the oxidizer having the smallest average particle size last, since the smallest particles have the highest surface to mass ratio and will scavenge the polyfunctional organic amine from the admixture. The order of mixing of ingredients as set forth can be varied. For example, when the polyfunctional amine additive reacts with the binder forming ingredients at a much faster rate than with the oxygen containing ammonium salt, it is generally preferable to add the polyfunctional amine after the oxidizer has been admixed with the binder forming ingredients.

The following examples will more fully illustrate this invention. All parts and percentages are by weight unless otherwise specified.

Examples 1-6

A binder solution is prepared by admixing 0.0108

parts of a chromium 2-ethylhexanoate catalyst containing 10.95 percent chromium into 7.727 parts of a carboxy-terminated polybutadiene having a molecular weight of about 6,000, and a carboxyl content of 1.48 to 1.53 equivalents per 100 grams of polybutadiene and containing 1.0 to 1.5 percent 2,2'-methylene-bis(4-methyl-6-tert-butyl) phenol as antioxidant. An epoxide crosslinking mixture is added in several increments with stirring after each addition. Two plasticizers comprising 1.906 parts dioctyl adipate and 1.906 parts of a random polymer of butadiene are then added to the binder mixture. The epoxide mixture is a solution of diepoxides having an epoxy equivalency of 156 and 89 percent pure, and a triepoxide having an epoxy equivalency of 103 and 99 percent pure. To this binder solution is added a polyfunctional amine as specified in Table I. The resulting admixture is agitated until the polyfunctional amine is completely dispersed and dissolved in the binder. Mixing time required is generally from about 15 - 20 minutes.

Following preparation of the binder mixture the solid ingredients are added as follows. Aluminum is added to the binder mixture and mixed for about 3 minutes. Ammonium perchlorate is added to the binder in three particle size ranges. Ammonium perchlorate having an average particle size of 200 μ and 400 μ is added to the binder and aluminum mixture and the resulting propellant matrix is agitated under a reduced pressure of 2.4 mm Hg for about 15 minutes. Ammonium perchlorate having an average particle size of 10 μ is then added to the propellant matrix and mixing is continued for an additional 15 minutes under a reduced pressure of 2.4 mm Hg. The resulting propellant is cast into a JANAF dogbone mold preheated at 180°F. The cast propellant is deaerated at reduced pressure of about 2.4 mm Hg for 1 hour. The propellant containing mold is sealed in a polyethylene bag containing a drying agent and the propellant is cured at 180°F. for 7 days. The cured propellant is cooled to ambient temperature and is cut into 0.25 inch thick dogbone test samples. These dogbones are stored over a drying agent at the testing temperature. These dogbones are tested for mechanical properties employing an Instron Tester at the temperatures set forth in Table II. Details of the binder composition, the polyfunctional amine employed, and the mechanical properties of the cured propellants are set forth in Table II. In each example a control propellant was prepared without the addition of polyfunctional amine and was tested for mechanical properties for comparison purposes.

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TABLE II

Propellant composition component	Wt. percent	Ex. 1		Ex. 2		Ex. 3		Ex. 4		Ex. 5		Ex. 6	
		TETA ¹	Control	TETA ¹	Control	TETA ¹	Control	TEPA ²	Control	PEI ³	Control	TETA ¹	Control
Ammonium perchlorate:		0.0135	0	0.0135	0	0.030	0	0.018	0	0.018	0	0.06	0
100 μ	20												
200 μ	32												
400 μ	31												
Aluminum, 10 μ	5												
Binder.....	12												
Ratio, epoxide/carboxyl (equivalents).....		1.02	1.02	1.03	1.03	1.03	1.03	1.07	1.07	1.02	1.02	1.02	1.02
Ratio, diepoxide/triepoxyde (equivalents).....		6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1
Mechanical properties (maximum stress) at 170° F.:													
Modulus (p.s.i.).....		422	330	388	350	308	350	384	460	41.9	380		
Tensile strength (percent).....		85	54	65	56	56	56	70	59	81	54		
Elongation (percent).....		33	23	40	21	39	21	22	17	29	23		
Mechanical properties (maximum stress) at 77° F.:													
Modulus (p.s.i.).....		787	520	710	560	450	560	681	700	779	520	160	520
Tensile strength (p.s.i.).....		127	83	97	96	82	96	114	103	119	83	26	83
Elongation (percent).....		37	33	48	31	47	31	28	27	96	33	26	33
Mechanical properties (maximum stress) at -40° F.:													
Modulus (p.s.i.).....				6,300	7,900	5,780	5,520						
Tensile strength (p.s.i.).....				387	500	407	316						
Elongation (percent).....				48	16	45	25						
Creep life at 77° F. and 65 p.s.i. initial stress: Time to failure (minutes).....				720	10	42	10						

¹ Triethylentetramine.² Tetraethylene pentamine.³ Polyethylamine is sold commercially under the trade name "Montrek 6" and has an average molecular weight of 600 and contains primary, secondary and tertiary amine groups in the ratio of 1:2:1.⁴ Strain rate of 0.074 in./in./min.⁵ Strain rate of 0.74 in./in./min.⁶ Strain rate of 74 in./in./min.

* Carboxylated rubber, 7.727; diepoxide, 0.391; triepoxide, 0.060; curing catalyst, 0.0108; hydrocarbon plasticizer, 1.906; ester plasticizer, 1.906.

Example 1 illustrates improved tensile strength and elongations for propellant containing triethylenetetramine as the polyfunctional amine. Microstructure failure analysis of this propellant shows failure of the

employing triethylenetetramine as the polyfunctional amine and following the general mixing procedure as set forth for Examples 1-6. Results of testing are set forth in Table III.

TABLE III

Propellant composition component	Weight percent	Ex. 7		Ex. 8		Ex. 9		Ex. 10		Ex. 11		Ex. 12	
		TETA ^{1,2}	Control	TETA ^{1,2}		TETA ^{1,2}	Control	TETA ^{1,2}		TETA ^{1,2}	Control	TETA ^{1,2}	
Amine additive.....	5	0.0135	0	0.030		0.0135	0	0.030		0.0135	0	0.030	
Ammonium perchlorate:													
12 μ.....	10												
200 μ.....	57												
400 μ.....	10												
Aluminum, 30 μ.....	1												
Molybdenum trioxide (MoO ₃).....	1												
Oxamide.....	4												
Binder*.....	13												
Ratio, epoxide/carboxyl (equivalents).....		1.03	1.03	1.03		1.05	1.05	1.05		1.07	1.07	1.07	
Ratio, diepoxide/triepoxide (equivalents).....		6.5/1	6.5/1	6.5/1		6.5/1	6.5/1	6.5/1		6.5/1	6.5/1	6.5/1	
Mechanical properties ³ (maximum stress) at 170° F.:													
Modulus (p.s.i.).....		388	348	308		452	533	428		298	398	419	
Tensile strength (p.s.i.).....		65	44	56		67	51	64		43	23	37	
Elongation (percent).....		40	23	39		34	16	34		53	46	58	
Mechanical properties ⁴ (maximum stress) at 77° F.:													
Modulus (p.s.i.).....		710	680	459		696	908	620		499	745	568	
Tensile strength (p.s.i.).....		97	86	82		101	84	93		87	85	86	
Elongation (percent).....		48	43	47		52	31	43		51	39	42	
Mechanical properties ⁵ (maximum stress) at -40° F.:													
Modulus (p.s.i.).....		6,300	5,520	5,780		5,190	8,330	6,643		5,853	6,643	6,680	
Tensile strength (p.s.i.).....		387	316	407		349	413	409		437	409	432	
Elongation (percent).....		48	25	45		41	10	22		31	22	26	
Creep life at 77° F. and 65 p.s.i. initial stress (hrs.).....		35	20 min.	3.5		48	20 min.	20		24	20 min.	13	
Mix viscosity (centipoises ×10 ³ at 140° F. at the end of propellant mixing).....		700	720	816		504	701	672		481	590	639	

¹ TETA is triethylenetetramine.

² All TETA containing propellants fail in the binder; all control propellants fail at the binder-filler interface.

³ Strain rate of 0.074 in./in./min.

⁴ Strain rate of 0.74 in./in./min.

⁵ Strain rate of 74 in./in./min.

*Carboxylated rubber, 8.626; diepoxide, 0.417; triepoxide, 0.064; catalyst, 0.079; hydrocarbon plasticizer, 1.882; ester plasticizer, 1.92.

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propellant in the binder phase, i.e., dewetting is substantially eliminated. Microstructure failure analysis of the control propellant at the same test conditions showed failure at the binder-filler interface illustrating dewetting.

Examples 2 and 3 illustrate improved tensile strengths, elongations, and improved creep properties compared to the control rounds. Propellants of Examples 2 and 3 employ triethylenetetramine as the polyfunctional amine and fail in the binder phase when subjected to high stress. The control propellants dewet i.e., fail at the binder-filler interface as determined by microstructure analysis when subjected to the same test.

Examples 4 and 5 illustrate improved elongation and tensile strengths of propellant compositions of this invention over the control propellants when employing tetraethylenepentamine and polyethyleneimine as the polyfunctional amine. The control propellants of Examples 4 and 5 dewet at the binder-filler interface as determined by microstructure analysis when subjected to the same testing conditions.

Example 6 illustrates the importance of concentration of the polyfunctional amine in achieving improvement in mechanical properties. When the percentage of triethylenetetramine is increased to 0.06 percent by weight, inferior mechanical properties result.

Examples 7-12

Six additional propellant compositions are prepared

Examples 7, 8, 9, 10, 11, and 12 (Table III) illustrate both improved tensile strengths and elongations from propellant prepared with triethylenetetramine as the polyfunctional amine and, in addition, the effect of concentration of triethylenetetramine on mechanical properties and mix viscosity. At 0.0135 percent concentration (Examples 7, 9, and 11) the tensile strength and elongation of the propellant is significantly better than at the 0.030 percent concentration level (Examples 8, 10, and 12) and resistance to creep failure is improved markedly. Also at the 0.0135 percent concentration level the mix viscosity is reduced significantly (Examples 9 and 11). At the 0.030 percent concentration level the mix viscosity is increased about 13 percent (Example 8) and about 8 percent (Example 12). The addition of 0.0135 percent triethylenetetramine in Example 9 reduced the mix viscosity 28 percent compared to the control sample and gave a propellant that appeared to have infinite creep life at 65 psi.

Examples 13-18

Six additional propellant compositions are prepared employing β-(4-aminophenyl)ethylamine (APE) as the polyfunctional amine following the general mixing procedure set forth for Examples 1-6. Propellant compositions and results of testing are set forth in Table IV.

TABLE IV

Propellant composition component	Ex. 13		Ex. 14		Ex. 15		Ex. 16		Ex. 17		Ex. 18	
	APE 1.2	Control	APE 1.2	Control	APE 1.2	Control	APE 1.2	Control	APE 1.2	Control	APE 1.2	Control
Amine additive	0.002	0	0.040	0	0.060	0	0.0113	0	0.0113	0	0.020	0
Ammonium perchlorate:												
20 μ												
200 μ												
400 μ												
Aluminum, 10 μ												
Binder												
Ratio, epoxide/carboxyl (equivalents)												
Ratio, diisocyanate/epoxide (equivalents)												
Mechanical properties ¹ (maximum stress) at 170° F.:												
Modulus (n.s.i.)	1.00	1.00	1.04	1.04	1.04	1.04	1.06	1.06	1.08	1.08	1.08	1.08
Tensile strength (n.s.i.)	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1	6.5/1
Elongation (percent)												
Mechanical properties ² (maximum stress) at 77° F.:												
Modulus (n.s.i.)	492	455	508	508	513	588	540	660	864	864	1,040	780
Tensile strength (n.s.i.)	101	80	116	86	86	98	102	172	172	140	140	100
Elongation (percent)	34	33	34	33	31	30	26	28	35	26	26	26
Mechanical properties ³ (maximum stress) at -40° F.:												
Modulus (n.s.i.)	6,770	7,400	7,280	8,000	7,080	8,000	10,100	7,800	9,160	8,610	8,100	500
Tensile strength (n.s.i.)	507	495	593	593	556	590	540	500	549	529	500	15
Elongation (percent)	17	17	31	31	33	33	14	14	48	48	48	20 min.
Creep life at 77° F. and 65 p.s.i. (initial stress) (hrs.)	21 min.	7 min.	48	48	5.5	20 min.	14	20 min.	570/150° F.	430/157° F.	20 min.	
Mix viscosity (centipoises) × 10 ³ at 140° F. at the end of propellant mixing	540/140° F.	650/140° F.	500/135° F.	528/140° F.	720/140° F.	600/141° F.						

¹ APE is 6-(4-aminophenyl)ethylamine.

² The APE containing propellants in Ex. 14-18 fail in the binder phase; the APE containing propellants fail at the binder-filler interface.

³ Strain Rate of 0.074 in./in./min.

⁴ Strain Rate of 0.74 in./in./min.

⁵ Strain Rate of 74 in./in./min.

*Carboxylated rubber, 7.727; diepoxide, 0.301; Triepoxide, 0.060; catalyst, 0.0108; hydrocarbon plasticizer, 1.906; ester plasticizer, 1.90.

Component	Weight %
50 Oxygen Containing Ammonium Salt	60-90
Cured Binder	5-20
Polyfunctional Organic Amine	0.005-0.05
Metal Fuel	0-20

Preferably, the propellant composition contains by weight from about 70 to about 90 percent oxidizer and from about 5 to about 20 percent cured binder. The cured binder includes the binder prepolymer and crosslinking agent. A curing catalyst is employed as needed. From about 40 to about 95 weight percent of the cured binder in the formulation is binder prepolymer, from about 1 to about 10 weight percent is the crosslinking agent, and the binder plasticizer can be from about 0 to about 50 weight percent, and preferably is from about 20 to about 40 weight percent of the binder.

The composite propellant of this invention can also contain other additives such as metal fuels, plasticizers, and the various compounding ingredients commonly employed in making composite propellants, as for ex-

Example 13 illustrates that at the 0.002 percent concentration level, APE has very little effect on mechanical properties or microstructural failure mode. This propellant and its control both fail at the binder-filler interface. However, at this low amine level the mix viscosity is reduced about 18 percent.

Examples 14 through 18 illustrate that at APE levels between 0.0113 and 0.060 percent, failure occurs exclusively in the binder phase whereas the corresponding control propellants fail at the binder-filler interface (dewetting). At these levels, resistance to creep failure is markedly improved.

Examples 14 and 15 illustrate that the upper limit of usefulness of APE appears to be about 0.060 percent in a diepoxide crosslinked carboxy-terminated rubber binder. At this concentration level (Example 15) the creep life is extended from 20 minutes (control) to 5.5 hours. At the 0.040 percent concentration level of Example 14, the propellant appears to have infinite creep life as evidenced by the fact that after 48 hours the rate of change of elongation with time is zero. The improvement in tensile strength and elongation is considerably greater at the lower (0.040 percent) APE concentration level. The mix viscosity is decreased significantly at both levels.

Example 16 illustrates that infinite creep life is obtained at APE concentration levels as low as 0.0113 percent.

Examples 17 and 18 illustrate that at an epoxide to carboxyl ratio of 1.08/1.0, somewhat better mechanical properties are obtained with APE concentration levels of 0.0113 percent (Example 17) than at 0.020 percent (Example 18). In both cases the resulting propellants appear to have infinite creep life.

All of the control propellants for Examples 1 through 18 fail the creep test at 77°F and 65 psi in less than 20 minutes. Conversely, the propellant compositions of this invention can be tailored to have a very long creep life as exemplified in Examples 9, 14, 16, 17 and 18.

The propellant compositions of this invention prepared in Examples 1-18 showed no porosity. While ammonia gas is liberated during mixing of the compositions, the amount of ammonia gas liberated is so small due to the small quantities of polyfunctional amine employed that substantially no porosity results.

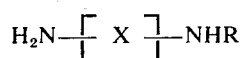
The propellant compositions of this invention have the following general compositions:

ample, oxidation inhibitors, reinforcing agents, wetting agents, surfactants, ballistic modifiers, radar attenuators, and the like. In this connection, metal fuels such as powdered aluminum, beryllium, magnesium, zirconium or boron, alloys such as the aluminum alloys of boron, magnesium, manganese, copper, and the like, and plasticizers such as dioctyl phthalate, dicytol azelate, dioctyl adipate, dodecyl adipate, polybutadiene, polyisobutylene, and the like can be utilized. Surfactants such as lecithin or mixtures of sorbitan monooleate and polyoxyethylene esters of mixed fatty and resin acids; ballistic modifiers such as di-n-butyl ferrocene, iron oxide, chromium oxide or oxamide, and radar attenuators such as molybdenum trioxide, can also be present in minor amounts in the propellant composition of this invention.

What I claim and desire to protect by Letters Patent is:

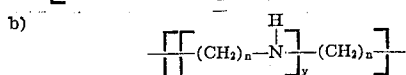
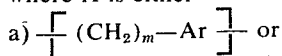
1. A composite propellant composition comprising in the form of a cured admixture:

- an oxidizer consisting essentially of an oxygen containing ammonium salt selected from the group consisting of ammonium perchlorate, ammonium nitrate, hydrazine perchlorate, hydrazine dperchlorate, and mixtures thereof,
- a crosslinkable binder prepolymer having reactive functional groups selected from the group consisting of hydroxyl, carboxyl and isocyanate groups and a crosslinking agent therefore said crosslinking agent having reactive functional groups selected from the groups consisting of polyepoxides, polyisocyanates, polythioisocyanates, and polyimines,
- a polyfunctional amine selected from the polyethyleneimine and amines having the general formula



(1)

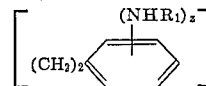
where X is either



wherein Ar is phenylene, amino-substituted phenylene, naphthylene, amino-substituted naphthylene; m is from 1 to 20; n is from 2 to 5; y is from 1 to 5; and R is hydrogen or a lower alkyl having from one to four carbon atoms,

said propellant composition comprising by weight from about 60 to about 90 percent of said oxygen containing ammonium salts, from about 5 to about 20 percent of crosslinkable binder prepolymer and crosslinking agent and from about 0.005 to about 0.05 percent of polyfunctional amine.

2. The composite propellant composition of claim 1 in which the polyfunctional amine is of the general formula (I) wherein X is



wherein z is 0, 1, 2, 3 or 4, and R₁ is hydrogen or lower alkyl having from one to four carbon atoms and R is hydrogen.

3. The propellant composition of claim 1 wherein the polyfunctional amine is triethylenetetramine.

4. The propellant composition of claim 1 wherein the polyfunctional amine is tetraethylenepentamine.

5. The propellant composition of claim 1 wherein the polyfunctional amine is diethylenetriamine.

6. The propellant composition of claim 1 wherein the polyfunctional amine is polyethyleneimine.

7. The propellant composition of claim 1 wherein the polyfunctional amine is β-(4-aminophenyl) ethylamine.

8. The composite propellant composition of claim 1 wherein the oxygen containing ammonium salt is ammonium perchlorate, the crosslinkable binder prepolymer is a carboxyl terminated prepolymer, and the crosslinking agent is a mixture of diepoxides and triepoxides.

9. The composite propellant composition of claim 8 wherein the polyfunctional amine is β-(4-aminophenyl) ethylamine.

10. The composite propellant composition of claim 1 wherein the oxygen containing ammonium salt is ammonium perchlorate, the crosslinkable binder prepolymer is a hydroxyl terminated prepolymer, and the crosslinking agent is a polyisocyanate.

11. The composite propellant composition of claim 1 wherein the oxygen containing ammonium salt is ammonium perchlorate, the crosslinkable binder prepolymer is a carboxyl terminated prepolymer, and the crosslinking agent is a polyimine.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,790,416 Dated February 5, 1974
Inventor(s) Henry C. Dehm

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9 & 10 - Table II;

Under Example 5, left hand column (labeled PEI³) the Modulus (p.s.i.) determined at 170°F should read 419, not 41.9 and,

The Elongation (percent) determined at 77°F should read 36, not 96.

Signed and sealed this 16th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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