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POLYURETHANE PROPELLANTS CONTAINING INORGANIC OXIDIZERS WITH ORGANO-SILICON COATING

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This invention relates to novel solid propellant compositions and in particular to such propellant compositions having superior castability, aging, and burning characteristics as well as lower temperature sensitivity. The propellants of this invention comprise a resin binder and a finely divided oxidizing agent having a surface coating of an organo-silicon material of a type more fully described below.

Solid propellant compositions are ordinarily composed of a resin fuel and an oxidizing material, the oxidizing material being intimately dispersed in the fuel. The ignition and burning properties of a propellant composition as well as its physical properties are dependent to a large extent upon the particular resins employed as fuels. In the novel propellant compositions of this invention, the preferred fuel is a cross-linked polyurethane which yields propellants of unexpectedly superior physical properties and performance characteristics.

The principal object of our invention is to provide a solid propellant material of lower temperature sensitivity which is less subject to premature ignition or detonation and safer to handle than propellants heretofore known.

Other objects and advantages of our invention will be apparent from the complete description thereof which follows.

The essence of our invention resides in our discovery that an extremely thin coating of an organo-silicon material, of a type more fully identified below, on the particles of a finely divided inorganic oxidizing salt results in a substantial improvement in the rheological properties of uncured solid propellant mixtures prepared therefrom. In addition, there results a superior propellant grain having safety and burning rate advantages not possessed by propellants identical thereto except that they contain uncoated oxidizer. Since the essence of our invention resides in the incorporation of coated oxidizing salts in solid propellant compositions, the invention is not limited to propellants in which the preferred polyurethane binders are employed but applies to solid propellants in general. Thus, the use of any well-known binder such as, for example, polyesteracrylate, rubber (butyl, polysulfide), etc., is within the scope of our invention.

In preparing the coated oxidizers of this invention, any well-known inorganic oxidizing material such as, for example, ammonium perchlorate, ammonium nitrate, or potassium perchlorate, in finely divided form, is treated with an organo-silicon coating agent of the class hereinafter disclosed so as to cause the deposit and adherence of a very thin film of organo-silicon material onto the surfaces of the oxidizer particles. Two means of treatment which have been found to accomplish these results are:

(1) Tumbling the oxidizer and organo-silicon coating agent together in a closed container for a predetermined period of time, and

(2) Stirring the oxidizer to be coated in a solution of the organo-silicon coating agent in a solvent such as toluene, benzene, pentane, etc., until thickening of the resulting slurry occurs and then removing the solids from the solution and effecting removal of the solvent therefrom by evaporation.

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Regardless of which of the above two preferred coating procedures is followed, the coated oxidizer is then preferably dried at about 180° F. for an adequate period of time, normally about one hour, to drive off any excess organo-silicon material. The coating technique identified as (1) will be referred to in this specification as the dry method and that identified as (2) will be referred to as the solution method.

The materials which we have found to be useful agents for the coating of finely divided oxidizers intended for use in the propellants of this invention are organo-silicon compounds having the general formula



wherein R is an alkyl, aryl, or alkenyl radical; X is a halogen or alkoxy radical; X' is a halogen or alkoxy radical; and Z is an alkyl, aryl, alkenyl, halogen, or alkoxy radical. These compounds are well-known to chemists and many references to them can be found in the literature. Typical examples of organo-silicon halides within the above-identified class of materials are methyl trichlorosilane, dimethyl dichlorosilane, ethyl tribromosilane, diethyl dibromosilane, ethyl trichlorosilane, diethyl dichlorosilane, butyl trichlorosilane, phenyl trichlorosilane, vinyl trichlorosilane, amyl trichlorosilane, allyl trichlorosilane, diallyl dichlorosilane, dimethyl diiodosilane, etc. For a disclosure of other organo-silicon halides suitable for use in our invention see U.S. Patent 2,788,280, granted April 9, 1957, to Rust et al.

Typical examples of organo-silicon compounds containing alkoxy groups which are suitable coating agents for our purpose are vinyl triethoxysilane, amyl triethoxysilane, phenyl triethoxysilane, methyl triethoxysilane, dimethyl diethoxysilane, amyl trimethoxysilane, etc. It is within the scope of this invention to employ mixtures of any of the aforesaid organo-silicon compounds if desired. Because of their ready availability and the superior results obtained therewith, the organo-silicons within the scope of the foregoing formula which are preferred for use in our invention are those having the formula



wherein R₁ is vinyl, phenyl or lower alkyl, such as methyl, ethyl or butyl.

While we do not know the exact thickness of the organo-silicon films on the coated oxidizers of this invention, we believe them to be extremely thin, having thicknesses something less than microns in order of magnitude. In view of this extreme thinness, it is difficult to see how their presence could have any noticeable effect on the properties of propellant mixtures and grains incorporating said coated oxidizers. However, we have made the unexpected discovery that the use of coated oxidizers of the type and for the purposes taught herein manifests itself in marked improvements in the properties of both uncured propellant mixtures and cured propellant grains. Thus, the incorporation of coated oxidizers into solid propellant compositions results in an increased fluidity and lowered viscosity, and an improved castability of the resultant propellant mixtures. As a result of the improved rheological properties of propellant mixtures containing the coated oxidizers, higher solids loadings are readily achieved. As those skilled in the art will appreciate, higher solids loadings is a result long sought after in the propellant art. Further, as pointed out above, a principal advantage of the use of coated oxidizers for purposes of this invention is the outstanding safety feature inherent

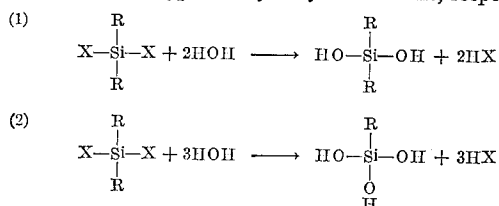
in the lowered temperature sensitivity of the cured propellants.

In preparing coated oxidizers for use in our novel propellants by either the dry method of solution technique, the quantity of organo-silicon coating agent should, for best results, be present in an amount ranging from about 1 percent, or less, to about 5 percent and preferably not greater than about 3 percent of the weight of oxidizer present. The weight of the organo-silicon film on the treated oxidizer is typically less than about 1 percent of the oxidizer weight and sometimes as low as 0.04 percent or even lower. For optimum results, where the oxidizer is ammonium perchlorate and the coating agent is vinyl trichlorosilane, the final coating should be present in an amount within the range from about 0.2 to about 0.6 percent of the oxidizer weight.

While either the dry method or the solution technique of applying the oxidizer coating works satisfactorily for our purpose, we have found the dry method to be the more feasible of the two for scale-up. Our novel invention is not limited to the use of oxidizers coated by any particular method and accordingly any suitably coated oxidizing salt, regardless of its method of preparation, is satisfactory for purposes of this invention.

While not bound by any theory as to the coating mechanism involved in this invention, we believe that the film on the coated oxidizer comprises a polymeric polysiloxane material. The polymeric siloxane material is the end product of a two-step reaction involving first hydrolysis of the organo-silicon coating agent followed by condensation of the hydrolyzed product; the hydrolysis being accomplished through the medium of the bound water present on the surface of the oxidizer. In the case of ammonium perchlorate, the residual surface moisture (bound water) is never less than about 0.03 percent by weight, this representing the surface moisture not removable by conventional drying processes.

Assuming that the coating mechanism of this invention takes place in the suggested manner, the organo-silicon coating agent is initially hydrolyzed to a dihydroxy or trihydroxy compound, depending upon the particular coating agent used. For example, if there are only two water reactive groups, e.g. halogen or alkoxy, in the coating agent, the product of hydrolysis will be a dihydroxy compound; if the starting material contains three water reactive groups the hydrolysis product will be a trihydroxy compound. The following general reaction schemes illustrate these two types of hydrolysis reactions, respectively:



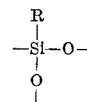
The R and X radicals in Equations 1 and 2 have the same meaning as set forth previously in the description of the organo-silicon coating agents of this invention. For simplicity's sake, the two R and the two X radicals in Equation 1 are indicated to be the same, as are the three X radicals in Equation 2. It is not essential that this be the case, however, and the X as well as the R radicals can be the same or different.

Continuing with the above hypothesis, after the polyhydroxy compound is formed by hydrolysis it condenses on the surfaces of the oxidizer particles to form an extremely thin coating of a silicone-type polymer containing a plurality of alternating silicon and oxygen atoms, each silicon atom being attached to at least one carbon atom. The polymeric silicone coatings have unit structures which are determined by the nature of the polyhydroxy monomers from which they are formed. Thus, where the polyhydroxy monomers are dihydroxy compounds, such as,

for example, dimethylsilicol or diphenyl silicol, the resulting polymeric silicones are thought to have the unit structure



which in the high molecular aggregate are of a linear character. The polymeric silicones may have as chain endings OH groups, which may react further, or $-\text{Si}(\text{R})_3$ groups which are unable to react further. Where the polyhydroxy monomers are trihydroxy compounds, as shown in Equation 2 above, the polymeric silicones condensed therefrom are thought to have the unit structure



and to be of a cross-linked nature. More detailed descriptions of polymeric silicones of the type hypothesized as the oxidizer coating can be found in U.S. Patent 2,258,218 to Rochow, granted October 7, 1941, and U.S. Patent 2,731,050 to Hyde, granted March 6, 1945.

In the production of composite propellants, such as those of this invention, resin fuel and oxidizer materials with various curing agents and combustion catalysts are normally blended into a slurry and then cast into a mold to form a propellant grain or cast directly into a rocket motor case to form a case-bonded grain. As indicated above, the preferred resin fuels for our propellants are the so-called polyurethane fuels, sometimes referred to as polyurethane binders.

The specific advantages of the polyurethane propellants of this invention containing the coated oxidizers are their improved burning rates and thermal stability.

The preferred polyurethane binders of our invention are prepared by reacting a compound having two or more active hydrogen containing groups, as determined by the Zerewitinoff method and capable of polymerizing with an isocyanate, with an organic compound having as the sole reacting groups two or more isocyanate or isothiocyanate groups. The compound having the active hydrogen groups is preferably an organic compound having as its sole reacting groups hydroxyl or thiol groups.

It will be apparent that, where there are more than two active hydrogen, isocyanate, or isothiocyanate groups present on any of the polyurethane reactants, the resulting molecular structure of the polyurethane binder will be at least to a certain extent of a cross-linked rather than a linear nature. The cross-linking is accomplished when all three functional groups of a sufficient number of the trifunctional molecules undergo the urethane reaction with other groups present in the mixture, thus resulting in a product having a "three-dimensional" molecular structure rather than mere aggregates of linear chains as is the case when bifunctional reactants are employed.

Where bifunctional reactants such as dihydroxy compounds and diisocyanates are employed to produce the polyurethane binders for our novel propellants, it is necessary to also employ a "cross-linking" agent to assure a product having the cross-linked structure essential to this invention. Cross-linking agents can also be used with polyurethane reactants having more than two functional groups such as triols or triisocyanates within the scope of this invention. Compounds suitable as cross-linking agents for our polyurethane binders are those organic compounds having as the sole reacting groups three or more groups polymerizable with hydroxy or isocyanate groups.

It will be appreciated that in any given batch of propellant the individual polyurethane molecules may vary in number of repeating units from several to tens of thousands of these units, hence molecular weight figures on

polyurethanes represent statistical averages. The exact nature of terminal groupings is not known and will vary depending upon whether plasticizers, polymerization catalysts, etc., are present. Moreover, a given molecule may even form a ring and thus leave no dangling radicals.

It is evident from the above that a wide variety of polyurethane binders for the propellants of this invention can be prepared by varying the particular isocyanate and hydroxy starting materials.

The isocyanate starting materials for our polyurethane binders are preferably diisocyanates but not necessarily so since, as explained above, other polyisocyanates (such as triisocyanates) or polyisothiocyanates may be employed within the scope of the invention if desired.

Our preferred diisocyanate compounds can be saturated or unsaturated; aliphatic or aromatic; open or closed chain; and, if the latter, monocyclic or polycyclic; and substituted or not by groups substantially unreactive with isocyanate or hydroxyl groups such as, for example, ketone, halogen, ester, sulfide, or other groups. The following diisocyanate compounds are particularly suitable as reactants for the preparation of binders for our novel polyurethane propellants.

- (a) Alkane diisocyanates such as:
Ethylene diisocyanate;
Trimethylene diisocyanate;
Propylene-1,2-diisocyanate;
Tetramethylene diisocyanate;
Butylene-1,3-diisocyanate;
Decamethylene diisocyanate;
Octadecamethylene diisocyanate; etc.
- (b) Alkene diisocyanates such as:
1-propylene-1,2-diisocyanate;
2-propylene-1,2-diisocyanate;
1-butylene-1,2-diisocyanate;
3-butylene-1,2-diisocyanate;
1-butylene-1,3-diisocyanate;
1-butylene-2,3-diisocyanate; etc.
- (c) Alkylidene diisocyanates such as:
Ethylidene diisocyanate;
Propylidene-1,1-diisocyanate;
Propylidene-2,2-diisocyanate; etc.
- (d) Cycloalkylene diisocyanates such as:
Cyclopentylene-1,3-diisocyanate;
Cyclohexylene-1,3-diisocyanate;
Cyclohexylene-1,2-diisocyanate;
Cyclohexylene-1,4-diisocyanate; etc.
- (e) Cycloalkylidene diisocyanates such as:
Cyclopentylidene diisocyanate;
Cyclohexylidene diisocyanate; etc.
- (f) Aromatic diisocyanates such as:
m-Phenylene diisocyanate;
o-Phenylene diisocyanate;
p-Phenylene diisocyanate;
1-methyl-2,4-phenylene diisocyanate;
Naphthylene-1,4-diisocyanate;
Diphenylene-4,4'-diisocyanate;
2,4-tolylene diisocyanate;
2,6-tolylene diisocyanate;
Durene diisocyanate;
4,4'-diphenylmethane diisocyanate;
1,5-naphthalene diisocyanate;
Methylene-bis-(4-phenylisocyanate);
2,2-propylene-bis-(4-phenylisocyanate);
Xylylene-1,4-diisocyanate;
Xylylene-1,3-diisocyanate;
4,4'-diphenylenemethane diisocyanate;
4,4'-diphenylene-propane diisocyanate; etc.

The preferred hydroxy starting materials for our polyurethane binders are dihydroxy compounds having the general formula $\text{HO}-\text{R}-\text{OH}$; where R is a divalent organic radical. The hydroxy groups on the above compounds can be of any type suitable for the urethane reaction with isocyanate groups such as, for example, alcohol

or phenolic hydroxy groups. The following dihydroxy compounds are particularly suitable as reactants for the polyurethane binders of this invention.

- (1) Alkane diols having a chain length of from 2 to 20 carbon atoms, inclusive, such as:
2,2-dimethyl-1,3-propanediol;
Ethylene glycol;
Tetramethylene glycol;
Hexamethylene glycol;
Octamethylene glycol;
Decamethylene glycol; etc.
- (2) Alkene diols such as:
1-propylene-1,2-diol;
2-propylene-1,3-diol;
1-butylene-1,2-diol;
3-butylene-1,2-diol;
1-hexylene-1,3-diol;
1-butylene-2,5-diol; etc.
- (3) Cycloalkylene diols such as:
Cyclopentylene-1,3-diol;
Cyclohexylene-1,2-diol;
Cyclohexylene-1,3-diol;
Cyclohexylene-1,4-diol; etc.
- (4) Aromatic diols such as:
Catechol;
Resorcinol;
Quinol;
1-methyl-2,4-benzenediol;
2-methyl-1,3-naphthalenediol;
2,4-toluenediol;
Xylylene-1,4-diol;
Xylylene-1,3-diol;
1,5-naphthalenedimethanol;
2-ethyl-1-phenyl-3-butene-1,2-diol;
2,2-di(4-hydroxyphenyl)propane; etc.

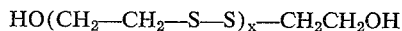
Other dihydroxy compounds suitable for the polyurethane reaction of this invention are polyesters such as those obtained from the reaction of a dihydric alcohol such as ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, or hexamethylene glycol with a dicarboxylic acid such as succinic acid, adipic acid, sebacic acid, oxadibutyric acid, sulfodipropionic acid, and related compounds. The polyesters most suitable for purposes of this invention are those having a molecular weight from about 1000 to about 2500. In preparing polyesters such as these, the dihydric component is permitted to react with the dicarboxylic acid component to produce the polyester. Mixtures of polyesters and an olefin such as styrene, vinyl acetate, or the like, are particularly suitable for purposes of this invention. The olefin does not react with any of the hydroxy groups present in the mixture, nor does it interfere in any way with the subsequent reaction between these hydroxyl groups and the isocyanate groups in the polyurethane reaction mixture. Neither does it interfere with any reactions of cross-linking agents present in the mixture. The principal function of the olefin is to permit linkage of the polyester molecules together through addition polymerization.

The above-mentioned polyesters can be prepared from either saturated or unsaturated dihydric alcohols and saturated or unsaturated dicarboxylic acids. The anhydrides of any of the dicarboxylic acids can be substituted for all or part of any of them in the preparation of polyesters suitable for the polyurethane reaction of our invention. The usual and preferred manner of making suitable polyesters is to react a mixture of an unsaturated dicarboxylic acid (such as adipic acid, sebacic acid, or the like) or anhydride and a saturated or aromatic dicarboxylic acid or anhydride with a dihydric alcohol. Examples of unsaturated dicarboxylic acids which can be employed are maleic acid, fumaric acid, citraconic acid, mesaconic acid, itaconic acid, etc.

In addition to the polyesters, polyethers such as polyethylene ether glycols, polypropylene ether glycols, other

polyalkylene ether glycols, and mixtures or copolymers thereof having molecular weights of from about 400 to about 10,000 can be utilized as dihydroxy reactants of the polyurethane reaction of this invention.

Polysulfides having two or more thiol groups, such as ethylene disulfide and the Thiokols produced by Thiokol Corporation, and polysulfides with glycol end groups such as those having the general formula



where x is a whole number, are other suitable reactants for the polyurethane reaction of our invention.

It will be appreciated by those skilled in the art that mixtures of suitable polyhydroxy and/or polyisocyanate compounds can be used for purposes of this invention if desired.

It is well-known to those skilled in the art that polyisothiocyanates and polythiol compounds react to yield urethane-type products as do the polyisocyanates and polyol compounds. Consequently, the polyisothiocyanates and polythiols corresponding to any of the polyisocyanates or polyhydroxy compounds taught herein can be employed for the preparation of propellant binders useful in this invention. For example, diisothiocyanates such as butylene-1,3-diisothiocyanate; ethylidene diisothiocyanate; cyclohexylene-1,2-diisothiocyanate; cyclohexylidene diisothiocyanate; p-phenylene diisothiocyanate; xylene-1,4-diisothiocyanate; etc.; react with dithiol compounds such as decamethylene dithiol; thioresorcinol; ethylene bis-(thioglycolate); etc.; to yield polythio-urethane compounds which are suitable as binders for our novel propellant compositions. Any mixture of the diisocyanates and/or diisothiocyanates suitable as reactants for the propellant binders of this invention can be reacted with any mixture of diols and/or dithiols disclosed as suitable for the purpose within the scope of our invention.

It will be appreciated by those skilled in the art that a great variety and number of polyfunctional organic compounds will serve as cross-linking agents for the polyurethane binders of this invention. As indicated above, any organic compound having as its sole reacting groups three or more groups polymerizable with hydroxy or isocyanate groups is a suitable cross-linking agent for purposes of this invention. This includes not only the obvious polyfunctional hydroxy, thiol, isocyanate, and isothiocyanate compounds but also compounds containing other groups polymerizable with either hydroxy or isocyanate groups. For example, compounds with three or more groups containing reactive hydrogen which are capable of polymerization with isocyanates can be employed as cross-linking agents within the scope of this invention. Examples of compounds of this class are proteins and synthetic polyamides such as polyhexamethylene adipamides. The cross-linking agents of this invention can be saturated or unsaturated; aliphatic or aromatic; open or closed chain and, if the latter, monocyclic or polycyclic; and substituted or not by groups substantially unreactive with isocyanate or hydroxyl groups such as, for example, ketone, halogen, ester, sulfide, or ether groups.

Examples of compounds which we have found to be particularly suitable as cross-linking agents are glycerol monoricinoleate; glycerol triricinoleate (referred to hereinafter as GTRO); 1,2,6-hexanetriol; methylene bis-(orthochloroaniline); monohydroxyethyl trihydroxypropyl ethylenediamine; polyaryl polyisocyanates; pentaerythritolpropylene oxide adduct; N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine; triethanolamine; trimethylolpropane; and triisocyanates such as toluene, 2,4,6-triisocyanate.

Other substances suitable as cross-linking agents are glycerol, sorbitol, dextrin, starch, cellulose, ethyl cellulose, cellulose acetate, polyvinyl acetals, polyvinyl ketals, polyvinyl alcohols, diethylenetriamine, polyvinyl mercaptans, and shellac.

As in the case of the polyurethane reactants, mixtures of the various cross-linking agents can be employed within the scope of this invention.

While polyurethane binders are preferred for purposes of this invention, it is within the scope of the invention to employ any other solid propellant binder in our novel propellants. For example, resinous binders such as asphalt, rubbers, polysulfides, rubber-polysulfide mixtures, resins, other combustible polymeric organic materials, etc., are all suitable for this purpose. Examples of combustible polymeric organic materials suitable as propellant binders are phenol-aldehyde resins, polyester resins, acrylate resins, and polyalkylene resins.

Examples of rubber binders which can be employed within the scope of our invention are polyisobutylene, butyl rubber, butadiene-styrene copolymers such as Buna-S, a butadiene-acrylonitrile copolymer such as Buna-N, highly polymerized vinyl alcohols in a plasticized state such as polyvinyl alcohol and chloroprene polymers such as Neoprene. The polysulfides suitable as solid propellant binders are exemplified by the Thiokols produced by Thiokol Corporation. The Thiokols are polyalkylene sulfides such as that resulting from the condensation of ethylene dichloride and sodium tetrasulfide. A more complete description of rubber and polysulfide propellant binders can be found in assignee's copending U.S. Patent No. 3,012,866, issued Dec. 12, 1961.

The so-called polyester resins suitable for use as solid propellant binders are formed by reacting a polyhydric alcohol with a polycarboxylic acid and copolymerizing therewith a monomeric olefinic component such as a vinyl, allyl, or other olefin compatible with the resin. To permit heteropolymerization between the polyester and olefin components, the polyesters are provided with some unsaturation through the incorporation therein of unsaturated polycarboxylic acid or anhydride and/or unsaturated polyhydric alcohol.

Saturated polycarboxylic acids useful in compounding the polyester resins are, for example, the aliphatic dibasic acids, including oxalic, malonic, succinic, glutaric, adipic, pimelic, sebacic, azelaic acids, etc., and the unsaturated carboxylic acids useful as the acidic components in forming polyester resins are maleic acid, fumaric acid, citraconic acid, mesaconic acid, itaconic acid, etc. The anhydrides such as itaconic anhydride and phthalic anhydride may likewise be used for supplying the desired unsaturation.

Regardless of which of the unsaturated acids are used, the degree of unsaturation necessary to provide cross-linkage with the vinyl, allyl, or other olefinic components may be obtained by the addition of any of the above-named unsaturated acids or their anhydrides.

The alcohols that can be used are not limited to the dihydric alcohols as other polyhydric alcohols such as the trihydric and higher polyhydric alcohols may be used. These afford additional possibilities for cross-linking and as a consequence, the toughness and brittleness of the final resin may be controlled as desired.

For the polyhydric alcohol component, any of the following alcohols may be used: dihydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, etc.; a trihydric alcohol such as glycerol; tetrahydric alcohols such as the erythritols, pentaerythritols, etc.; pentitols which include arabitol, adonitol, xylitol, etc.; hexitols including mannitol, sorbitol, dulcitol, etc.; heptitols such as persitol, volamitol, etc.; or mixtures of any of the above alcohols may be also employed if desired.

The olefinic component of the polyester resin binders may be styrene; vinyl acetate; acrylic acid esters; methacrylic acid esters; allyl compounds such as allyl diglycol carbonate, diallyl maleate, and diallyl glycolate; and other unsaturated components such as propylene, butadiene, etc.; as well as derivatives of any of the above substances which are capable of polymerization with the resin. In general, any olefin which will polymerize with the resin to

form a solid grain may be employed; this includes all unsubstituted olefins and in addition many substituted olefins.

The polyester resins suitable as propellant binders and their methods of preparation are more fully disclosed in assignee's U.S. Patent No. 3,031,288, issued April 24, 1962.

Acrylate resin binders within the scope of this invention comprise copolymers of any two or more reduced oxygen-containing polymerizable monomers such as alkenoic acids, alkenoic acid esters, dialkenyl diglycolates, dialkylene diglycol bis-(alkenyl carbonate), alkenyl phthalates, etc. Examples of reduced oxygen-containing polymerizable monomers suitable for acrylate propellant binder formation are the acrylates and methacrylates such as methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, butyl methacrylate, propyl methacrylate, diethylene glycol bis-(allyl carbonate), glycidol allyl ether, diallyl phthalate, diallyl diglycolate, diallyl maleate, diallyl fumarate, etc.

Other acrylate binders suitable for use in our invention are prepared by copolymerizing polymerizable substances containing unreduced oxygen in the molecule, such as the nitro and nitroether-substituted alkenoic acids and esters. Specific examples of nitro-containing monomers which copolymerize to form acrylate propellant binders are 2-nitroethyl acrylate; the nitrobutyl acrylates; 2,2-dinitropropyl acrylate; 2,2,3,3-tetranitrobutyl acrylate; and 2,2,3,3-tetranitrobutyl methacrylate.

Still other acrylate binders comprise copolymers of any one or more of the above-mentioned reduced oxygen-containing monomers and any one or more of the above-mentioned monomers containing unreduced oxygen in the molecule. These binders, as well as those acrylate binders referred to above, and their methods of preparation are more fully described in assignee's copending U.S. patent application Serial No. 321,941, filed November 21, 1952, and now abandoned.

Polyurethane resins containing unreduced oxygen are suitable binders for the propellants of our invention. Such binders can be prepared by condensing nitro-containing isocyanates and nitro-containing alcohols, as more fully disclosed in assignee's copending U.S. patent application Serial No. 728,491, filed April 14, 1958.

In the preparation of the nitro-substituted polyurethanes of application Serial No. 728,491, both the alcohol and isocyanate starting materials may contain nitro groups. However, this is not necessary and it is sufficient if the nitro groups are initially present on only an alcohol or isocyanate starting material. The nitro-substituted polyurethanes (hereinafter referred to as nitropolyurethanes) can be cross-linked or not as desired.

Polyurethane propellants can be prepared with any degree of nitro saturation but it is cautioned that only those binders sufficiently deficient in oxygen to require the presence of an oxidizer salt for satisfactory propellant utility are employed in the propellants of this invention. The reason for this is the fact that the essence of the present invention resides in the use of a coated oxidizing salt of unique characteristics.

Examples of alcohols useful for the preparation of nitropolyurethane propellant binders are lower alkylene diols such as ethylene glycol, 1,3-propanediol, and 1,2-pentanediol; nitroalkylene diols such as 2-methyl-2-nitro-1,3-propanediol, 4,4,6,8,8-pentanitro-1,11-undecanediol, 2,2,4,4-tetranitro-1,5-pentanediol, 4,4,6,6,8,8-hexanitro-1,1,1,1-undecanediol, 5,5,5-trinitro-1,2-pentanediol, 5,5-dinitro-1,2-hexanediol, and 2,2-dinitro-1,3-propanediol; nitrazaalkylene diols such as 3-nitrazo-1,5-pentanediol, 3,6-dinitraza-1,8-octanediol, and 2-nitrazo-1,4-butanediol; and nitrazanitroalkylene diols such as 5-aza-3,3,5,7,7-pentanitro-1,9-nonanediol and 6-aza-3,6-dinitro-1,8-octanediol.

Examples of isocyanates useful as starting materials for the preparation of nitropolyurethane propellant binders are lower alkylene diisocyanates such as methylene diisocyanate, ethylene diisocyanate, and 1,3-propane diisocyanate; nitroalkylene diisocyanates such as 3,3-dinitro-

1,5-pentane diisocyanate, 3,3,5,7,7-pentanitro-1,9-nonane diisocyanate, 2,2,4,4-tetranitro-1,5-pentane diisocyanate, and 5,5,5-trinitro-1,2-pentane diisocyanate; nitrazaalkylene diisocyanates such as 3,6-dinitraza-1,8-octane diisocyanate, 3-nitrazo-1,5-pentane diisocyanate, and 2-nitrazo-1,4-pentane diisocyanate; and nitrazanitroalkylene diisocyanates such as 5-aza-3,3,5,7,7-pentanitro-1,9-nonane diisocyanate, 6-aza-3,6-dinitro-1,8-octane diisocyanate, and 5-aza-3,3,5-trinitro-1,9-nonane diisocyanate.

Mixtures of any of the above-named alcohols and isocyanates can be polymerized to form propellant binders within the scope of this invention.

Illustrative of other solid propellant binders suitable for use in the novel propellants of our invention are those disclosed in U.S. Patent 2,479,828 and British Patent 579,057.

The oxidizers of this invention can be any solid inorganic oxidizing salt, numerous of which are well-known to those skilled in the art. Examples of suitable oxidizing salts are the chromates, dichromates, permanganates, nitrates, chlorates, and perchlorates of the alkali or alkaline earth metals (such as potassium, sodium, ammonium nitrate and ammonium perchlorate, calcium and the like); ammonia; hydrazine; or guanidine.

The selection of the oxidizing salt depends upon the specific burning properties desired in the propellant grain. Thus, where a substantially smokeless propellant is desired, a nonmetallic oxidizing salt such as ammonium perchlorate or ammonium nitrate should be employed rather than an oxidizing salt containing a metal such as sodium nitrate, potassium perchlorate, or calcium chlorate. Mixtures of suitable inorganic oxidizing salts can be used within the scope of this invention.

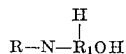
Various additives can be employed in preparing the polyurethane binders of this invention. Typical plasticizers are isodecyl pelargonate; 4-nitrazapentanitrile; 2,2-dinitropropyl-4-nitrazapentanoate; di-(2-ethylhexyl) azelate, and the like. Also, catalysts for the polyurethane reaction such as triethylamine and other tertiary amines, ferric acetylacetonate and other metal acetylacetonates such as vanadyl acetylacetonate, etc.; boron trifluoride, etc., can be employed. The catalysts can be employed in quantities ranging from mere traces up to amounts equivalent to about one percent by weight of the total propellant mass, and higher. Catalyst quantities from about 0.02 to about 0.10 percent by weight, on a total weight basis, are, however, generally employed.

The polymerization reaction can be carried out in a suitable solvent or in the absence of a solvent. The solvent can be present in such great excess as to form a solution of the monomers or it can be used in a relatively small quantity. Suitable solvents such as 4-nitrazapentanoate, dioxane, dimethylphthalate, etc., are non-reactive with the various propellant ingredients and further are capable of solubilizing these ingredients.

Other additives such as antioxidants, wetting agents, anti-foaming agents, etc., can be employed if desired in the formulation of our novel propellants. For example, in order to overcome porosity due to gasification in our novel propellant formulations, a silicone oil can be added as an antifoaming agent to the propellant mix. The use of silicone oils as antifoaming agents in our propellant mixes results in improved processing, reduces foaming of the propellant ingredients during mixing, aids in vacuumization of the mix, and reduces porosity in the cured propellants. A preferred silicone oil antifoaming agent is polydimethylsiloxane of approximately 1000 centistokes viscosity such as that available commercially under the trade name Linde L-45. Antifoaming agents are added to the propellant mix in small quantities, normally in an amount not greater than about 0.01 percent by weight of the mix.

We have found certain well-known wetting agents such as lecithin to be useful processing aids in the preparation of our novel propellants. A wetting agent which we have

found to be particularly suitable for our purpose is that known commercially as G-2684, a mixture of sorbitan monooleate and polyoxyethylene esters of mixed fatty and resin acids. Other wetting agents useful for our purpose are materials having the general formula



wherein R is an aliphatic 17 to 24 carbon group and R₁ is a polypropylene oxide group. An example of this type of agent is that known commercially as Priminox-10. Still other suitable wetting agents for use in our novel propellants are sorbitan trioleate and the polyoxyethylene sorbitan monolaurates.

A product representative of the latter class of materials is available on the commercial market under the trade name Tween 21. As is well-known to those skilled in the art, wetting agents, or as they are sometimes called, surface active agents, are useful in improving the processibility and castability of solid propellant mixes. For best results we have determined that wetting agents should be incorporated into our novel propellant formulations in proportions not greater than about 1 percent by weight, on a total weight basis, and preferably in amounts substantially lower than this.

It is within the scope of our invention to employ mixtures of the various wetting agents and other additive ingredients in our novel propellant compositions.

In addition to the above-mentioned additives there are numerous others which can be employed in minor amounts within the scope of our invention. For example, as indicated above, materials useful as anti-oxidants can be utilized in the propellants of this invention and one such material which we have found to be particularly suitable for that purpose is N,N'-diphenyl-p-phenylenediamine.

In addition to those additives which are added in minor amounts to our novel propellants there are other non-critical ingredients which can be employed within the scope of this invention. For example, it is within the scope of the invention to incorporate finely divided aluminum in amounts up to about 40 percent by weight (or higher) into the propellants, the preferred quantity being in the neighborhood of about 10 to about 26 percent by weight, on a total propellant weight basis.

The aluminum improves the tensile properties of propellants by acting as a reinforcing constituent in a manner somewhat analogous to the action of aluminum powder as a filler in adhesives to improve the strength of the glue line. In addition, the aluminum powder occupies a smaller volume than other propellant ingredients, providing more fuel between particles. The use of aluminum also permits a lower oxidizer concentration which results in a higher fuel content. Increasing fuel content yields higher values of elongation at low temperatures resulting in less tendency to crack or fail during temperature cycling. Examples of commercially available aluminum powders which are suitable for our purpose are Alcoa grade 120, having an average particle size of 76μ, Reynolds grade 1-511, having an average particle size of 40μ, and Reynolds grade 400, having an average particle size of 7μ.

Preferably, the propellants of this invention have an oxygen balance of from about +20 to -60, based on the conversion of all of the hydrogen, carbon and metal (if present) to water, carbon dioxide and metal oxide respectively.

In preparing the polyurethane propellants of this invention, the polyurethane polymerization can be conducted at any temperature, the only effect of temperature variation being a corresponding increase or decrease in the rate of reaction. The polymerization readily takes place at room temperature but higher temperatures increase the rate of reaction and are therefore desirable in many cases. However, temperatures lower than room temperature can also be used for our polymerization reaction.

Because higher temperatures tend to produce shrinkage and internal strains, it is preferable to carry out the cure at temperatures in the range of from about 70° to about 180° F. Within this range, reaction is sufficiently rapid for economical production; yet the temperature is not so high as to produce shrinkage and internal stresses which are especially harmful in the case of large solid propellant motors.

Those skilled in the art will appreciate the fact that heating and cooling steps can be incorporated into our propellant processing procedure for various reasons, such as to attain optimum operating conditions. Likewise, various other techniques which serve to optimize the processing procedure or improve the quality of the product (such as vacuumizing the mixture during certain phases of the operation) can be employed in the practice of this invention if desired.

The various processing steps of this invention can be carried out with standard equipment well-known to those skilled in the art as suitable for the purpose. A mixer which we found to be particularly effective for mixing our propellant ingredients, however, is that known commercially as the P mixer. The P mixer is manufactured by Baker-Perkins, Inc., of Saginaw, Michigan, and it can be equipped with facilities for heating, cooling, and vacuumizing propellant batches during mixing for use where such facilities appear to be warranted.

After the propellant batch has been mixed to substantial uniformity, it is cast, extruded, or compression-formed to the desired shape and cured at a temperature preferably within the range from about 70° to about 180° F. As pointed out above, the propellant mixture can also be cast directly into a rocket chamber lined with an inert liner material and polymerized (cured) therein.

There are many ways of processing the various ingredients used in the formulation of our propellants. For example, where the polyurethane reactants are diols and diisocyanates, and the cross-linkers are polyhydroxy compounds, the diol can be first mixed with the cross-linker, after which the inorganic oxidizer and the diisocyanate can be stirred or otherwise mixed into the mass. Catalysts and/or other additives can be introduced into the mixture prior to, at the same time, or subsequent to the addition of the diisocyanate. The various additives do not all have to be added at the same stage of processing; in fact, it has been found preferable in most cases to deviate from such a procedure. One technique which we have found to be quite satisfactory (where the major ingredients and order of addition of these ingredients are as described above) comprises first the addition of a wetting agent or agents, and the plasticiser, to the diol and cross-linker in the mixer; followed by the addition of the burning rate modifiers (such as copper chromite and carbon black) during addition of the inorganic oxidizer; and subsequently the addition of the curing catalyst (such as ferric acetylacetonate) along with addition of the diisocyanate. Modifications of the above methods of introducing the additives, such as, for example, addition of the wetting agents to the diol prior to introduction into the mixer, are varied and many. Likewise, there are many techniques for processing the major components in the preparation of our novel propellants. For example, the diol can first be mixed with the inorganic oxidizer, after which the diisocyanate can be added, along with the catalyst and cross-linker.

From about 45 to about 95 weight percent of oxidizer, based on the total weight of the final propellant, is preferably employed in the preparation of our novel solid propellants. The amount of binder, or fuel, is therefore preferably employed in an amount within the range from about 55 to about 5 percent by weight of the product. By fuel, as the term is used herein, is meant the polyurethane binder which comprises not only the diol (or equivalent) and the diisocyanate (or equivalent) but any cross-linker present as well.

The proportions of the ingredients which go to make up the fuel can vary through wide ranges, depending on the properties desired in the propellant and the specific reactants employed. Although stoichiometric proportions of hydroxy and isocyanate components can be employed in the preparation of our novel solid propellants, we have found that a product of improved mechanical properties is obtained if a slight excess of isocyanate groups over hydroxy groups is present in the fuel mixture. Consequently, for best results we have found that there should be from about 100 to about 115 equivalents of isocyanate or isothiocyanate containing monomer in the fuel mixture for every 100 equivalents of hydroxy or thiol containing monomer.

There can, of course, be more than one isocyanate compound, or equivalent, as well as more than one hydroxy compound, or equivalent, in the fuel mixture. In this case the calculation of excess isocyanate over hydroxy groups is based upon the total amounts of all cyanate and hydroxy compound present. For example, where the cross-linker is a polyhydroxy compound the excess of isocyanate compound (or equivalent) is calculated as an excess over the sum of the amount of diol (or its equivalent) plus the amount of cross-linker. The relative proportions of diol and cross-linker can vary through wide ranges so long as a cross-linked structure in the fuel results therefrom.

The various additives and minor components of our novel propellants (that is, those ingredients other than the urethane and cross-linker reactants) normally comprise a very small percentage of the total propellant weight. Thus, they will usually be present in combined amount not greater than about 10 percent (and preferably about 4 or 5 percent) of the total propellant weight.

Our novel solid propellants can be used as the primary propulsion source in rocket-propelled vehicles or as a propellant for artillery missiles. When used as the primary propulsion source for rocket vehicles, they can be conveniently ignited by a conventional igniter, as for example, the igniter disclosed in assignee's U.S. Patent No. 3,000,312, issued September 19, 1961. The propellant is preferably cast directly in the rocket chamber in which it is to be fired and restricted on one or both ends in the conventional manner with a relatively slow burning inert resin, such as a polyurethane or a polyester resin. The restriction is preferably accomplished by applying a relatively thin coating of the inert resin to the inner surfaces of the rocket chamber lining prior to casting the propellant therein. Rocket chambers such as those in which our novel solid propellants are employed are ordinarily of the conventional type having one end open and leading into a venturi rocket nozzle. Upon ignition, large quantities of gases are produced and exhausted through the nozzle to create propulsive force.

In order to further illustrate our invention there are presented the following examples in which all parts and percentages are by weight unless otherwise indicated.

Example I

One pound of NH_4ClO_4 containing about 0.03 percent surface moisture was added to a stirred solution of 9.1 grams of vinyltrichlorosilane in 200 ml. of toluene. Mixing was continued until thickening of the slurry occurred. The wet NH_4ClO_4 slurry was then transferred to an evaporating dish and the wet particles were stirred with a spatula at periodic intervals for about half an hour after which time essentially all of the solvent had evaporated. The coated material was dried at 180°F . for one hour to drive off any unreacted vinyltrichlorosilane. The dry coated NH_4ClO_4 , as produced by the solution technique, was sieved through a 30-mesh screen.

The coated NH_4ClO_4 remained free-flowing after a number of weeks of storage under ambient conditions. In contrast, uncoated NH_4ClO_4 showed excessive caking when subjected to like conditions.

The bulk density of the coated NH_4ClO_4 was determined and compared to that of uncoated NH_4ClO_4 . Briefly, the method of determining bulk density comprised filling a 100 cc. graduate with the sample to be tested; vibrating the filled graduate on a vibrator for five minutes and then noting the volume; continuing to vibrate at five-minute intervals until no further decrease in volume occurred, and then weighing the sample and determining its bulk density in grams per cubic centimeter (gm./cc.). Comparative data on uncoated NH_4ClO_4 and the coated NH_4ClO_4 of this example were as follows.

Sample:	Bulk density (gm./cc.)
Uncoated -----	1.18
Coated -----	1.38

The above results show that the uncoated material is increased in bulk density by 17 percent by coating it as described in this example.

An increase in the bulk density of oxidizer through coating results in improved castability of the propellant mix containing the coated oxidizer. As pointed out above, an increase in bulk density indicates that higher solids loadings in propellants can be achieved. Higher solids loadings are desirable in that, inter alia, they result in improved rheological properties of the propellant mix. It is felt that the improvement in the rheological properties of propellant mixes containing coated oxidizers can be attributed, at least partly, to an increased wetting of the oxidizer particles as a result of their coated surfaces.

Example II

To illustrate the dry method for coating the oxidizer, one pound of ammonium perchlorate is tumbled with 0.5 percent by weight of vinyltrichlorosilane for approximately 45 minutes in a closed glass container. The coated oxidizer is dried by heating, as described in Example I, to produce a free-flowing powder. To 60 parts of this coated oxidizer, are added 100 parts of an isobutylene-butadiene copolymer having a molecular weight of about 150,000 and an iodine number of about 50. This mixture is cured with about 5 parts sulfur to obtain a rubbery solid propellant.

Example III

A sample of coated ammonium perchlorate was prepared by the solution technique described in Example I using vinyltrichlorosilane as the coating agent. The coating (presumed to be vinylpolysiloxane) was found to be present on the oxidizer in an amount equivalent to about 0.4 percent of the oxidizer weight.

Two batches of propellant mix were prepared which were the same except that the coated oxidizer was employed in one batch and uncoated oxidizer was employed in the other batch. The formulation (which is the same for both batches) is given below.

Ingredient:	Weight percent
Polyurethane binder -----	24.50
NH_4ClO_4 -----	75.00
Neozone D -----	0.25
Ferric acetylacetonate -----	0.07
Tween 21 -----	0.18
	100.00

In the above formulation, the polyurethane binder was prepared by mixing polypropyleneglycol, having a molecular weight of 2025, 2,4-toluene diisocyanate, and trimethylolpropane in the following equivalent percent ratio of monomers: 70/107/30. The polypropylene glycol and 2,4-toluene diisocyanate were the primary polyurethane ingredients and the trimethylolpropane was present as a cross-linking agent. Neozone D is a trade name for phenyl betanaphthylamine, which was employed as an antioxidant. Ferric acetylacetonate is a catalyst for the

polyurethane reaction and Tween 21 is a polyethylene sorbitan monolaurate, and serves as a wetting agent.

Cured samples of the two batches of propellant mix, one containing the coated and the other containing uncoated oxidizer, were prepared. The samples were prepared by mixing the propellant ingredients to a uniform consistency and heating the mixture to about 110° F. to cure the binder. During the processing of the two samples, it was found that the mix containing the coated oxidizer was more fluid and easier to cast than was the mix containing the uncoated oxidizer.

The procedures of mixing and casting are more fully described in assignee's copending U.S. application, Serial No. 829,180, filed July 20, 1959.

Other propellants containing the coated oxidizers of this invention are prepared as follows.

Example IV

Ingredient:	Weight percent
Sodium nitrate (coated with a polymer of methyl trichlorosilane using the solution method described in Example I) -----	80.00
2,4-tolylene diisocyanate -----	7.45
Decamethylene glycol -----	10.25
2,4,6-tolylene triisocyanate -----	2.30
	100.00

Example V

Ingredient:	Weight percent
Potassium nitrate (prepared by the dry method described in Example II using amyl trichlorosilane as the coating agent) -----	82.00
Propylene glycol (mol. wt. 2025) -----	14.73
2,4-tolylene diisocyanate -----	2.12
Glycol triricinoleate -----	1.15
	100.00

Example VI

Ingredient:	Weight percent
Ammonium nitrate (prepared by the solution technique of Example I, using phenyl trichlorosilane as the coating agent) -----	80.00
Polytetramethylene ether glycol (M.W.=3000) -----	17.45
Hexamethylene diisocyanate -----	2.20
N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine -----	0.35
	100.00

Having described our invention, it is intended that the invention only be limited by the lawful scope of the appended claims.

We claim:

1. A solid propellant composition which comprises a cured intimate mixture of a nonmetallic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an organo-silicon material selected from the group consisting of compounds having the general formula



and mixtures thereof, wherein R is a radical selected from the group consisting of alkyl, aryl, and alkenyl radicals; X is a radical selected from the group consisting of halogen and alkoxy radicals; X' is a radical selected from the group consisting of halogen and alkoxy radicals; and Z is a radical selected from the group consisting of alkyl, aryl, alkenyl, halogen, and alkoxy radicals; and a resin binder.

2. A solid propellant composition which comprises a cured intimate mixture of a solid inorganic oxidizing salt having a surface coating adherent thereto, said surface

coating having been obtained by treatment of said oxidizing salt with an organo-silicon material selected from the group consisting of compounds having the general formula



and mixtures thereof, wherein R is a radical selected from the group consisting of alkyl, aryl, and alkenyl radicals; X is a radical selected from the group consisting of halogen and alkoxy radicals; X' is a radical selected from the group consisting of halogen and alkoxy radicals; and Z is a radical selected from the group consisting of alkyl, aryl, alkenyl, halogen, and alkoxy radicals; and a cross-linked resin binder which comprises the reaction product of a compound having, as its sole reacting groups not less than two active hydrogen groups as determined by the Zerevitinoff method, polymerizing with an isocyanate, and a compound having, as its sole reacting groups, not less than two groups capable of undergoing a urethane-type reaction with active hydrogen groups.

3. A solid propellant composition which comprises a cured intimate mixture of a nonmetallic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an organo-silicon material selected from the group consisting of compounds having the general formula



and mixtures thereof, wherein R is a radical selected from the group consisting of alkyl, aryl, and alkenyl radicals; X is a radical selected from the group consisting of halogen and alkoxy radicals; X' is a radical selected from the group consisting of halogen and alkoxy radicals; and Z is a radical selected from the group consisting of alkyl, aryl, alkenyl, halogen, and alkoxy radicals; a resin binder; and aluminum.

4. A solid propellant composition which comprises a cured intimate mixture of a nonmetallic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an organo-silicon material selected from the group consisting of compounds having the general formula



and mixtures thereof, where R is a radical selected from the group consisting of alkyl, aryl, and alkenyl radicals; X is a radical selected from the group consisting of halogen and alkoxy radicals; X' is a radical selected from the group consisting of halogen and alkoxy radicals; and Z is a radical selected from the group consisting of alkyl, aryl, alkenyl, halogen, and alkoxy radicals; a cross-linked resin binder which comprises the reaction product of a compound having, as its sole reacting groups, not less than two active hydrogen groups capable of polymerizing with an isocyanate and a stoichiometric excess of a compound having, as its sole reacting group, not less than two groups capable of undergoing a urethane-type reaction with hydroxy groups, said stoichiometric excess being calculated as an excess over all active hydrogen groups capable of polymerizing with an isocyanate initially present.

5. The solid propellant composition of claim 4 wherein said stoichiometric excess of reactant material containing groups capable of undergoing a urethane-type reaction with hydroxy groups over the reactant material containing active hydrogen groups capable of polymerizing with an isocyanate corresponds to a proportion of from about 100 to about 115 equivalents of the former for every 100 equivalents of the latter.

6. A solid propellant composition which comprises a cured intimate mixture of a nonmetallic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an organo-silicon material selected from the group consisting of compounds having the general formula



and mixtures thereof, wherein R_1 is a radical selected from the group consisting of lower alkyl, aryl, and vinyl radicals; and a resin binder which comprises the reaction product of a compound having two active hydrogen groups capable of polymerizing with an isocyanate selected from the group consisting of

- (a) alkane diols having a chain length of from 2 to 20 carbon atoms, inclusive;
- (b) alkane dithiols having a chain length of from 2 to 20 carbon atoms;
- (c) alkene diols;
- (d) alkene dithiols;
- (e) cycloalkylene diols;
- (f) cycloalkylene dithiols;
- (g) aromatic diols;
- (h) aromatic dithiols;
- (i) dihydroxy polyesters having a molecular weight from about 1000 to about 2500;
- (j) polyalkylene ether glycols having a molecular weight from about 400 to about 10,000;
- (k) polysulfides with glycol end groups; and mixtures thereof;

a compound selected from the group consisting of:

- (1) alkane diisocyanates;
- (2) alkane diisothiocyanates;
- (3) alkene diisocyanates;
- (4) alkene diisothiocyanates;
- (5) alkylidene diisocyanates;
- (6) alkylidene diisothiocyanates;
- (7) cycloalkenylene diisocyanates;
- (8) cycloalkenylene diisothiocyanates;
- (9) cycloalkylidene diisocyanates;
- (10) cycloalkylidene diisothiocyanates;
- (11) aromatic diisocyanates;
- (12) aromatic diisothiocyanates; and mixtures thereof;

and, as a cross-linking agent, a compound having as its sole reacting groups, not less than 3 groups polymerizable with a group selected from the class consisting of hydroxy, thiol, isocyanate and isothiocyanate groups.

7. The solid propellant composition of claim 6 wherein the resin binder comprises the reaction product of from about 100 to about 115 equivalents of the compound selected from the group consisting of

- (1) alkane diisocyanates;
 - (2) alkane diisothiocyanates;
 - (3) alkene diisocyanates;
 - (4) alkene diisothiocyanates;
 - (5) alkylidene diisocyanates;
 - (6) alkylidene diisothiocyanates;
 - (7) cycloalkylene diisocyanates;
 - (8) cycloalkylene diisothiocyanates;
 - (9) cycloalkylidene diisocyanates;
 - (10) cycloalkylidene diisothiocyanates;
 - (11) aromatic diisocyanates;
 - (12) aromatic diisothiocyanates;
- and mixtures thereof;

for every 100 equivalents of said compound having two active hydrogen groups capable of polymerizing with an isocyanate plus said cross-linking agent.

8. A solid propellant composition which comprises a cured intimate mixture of a nonmetallic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with a vinyl trihalosilane; and a resin binder which comprises the reaction product of an aromatic diisocyanate, a polyether having a molecular weight from about 400 to about 10,000, and a trihydroxy cross-linker compound; said coated inorganic oxidizing salt being present in an amount between about 45 and about 95 percent by weight of said propellant composition, and said resin binder being present in an amount between about 55 and about 5 percent by weight of said propellant composition.

9. A solid propellant composition which comprises a cured intimate mixture of a nonmetallic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an alkyl trihalosilane; and a resin binder which comprises the reaction product of an aromatic diisocyanate, a polyether having a molecular weight from about 400 to about 10,000, and a trihydroxy cross-linker compound; said coated inorganic oxidizing salt being present in an amount between about 45 and about 95 percent by weight of said propellant composition, and said resin binder being present in an amount between about 55 and about 5 percent by weight of said propellant composition.

10. The propellant composition of claim 8 wherein said trihydroxy cross-linker compound is glycerol monoricinoleate.

11. A solid propellant composition which comprises a cured intimate mixture of ammonium perchlorate having a surface coating adherent thereto, said surface coating having been obtained by treatment of said ammonium perchlorate with vinyl trichlorosilane; and a resin binder which comprises the reaction product of 2,4-tolylene diisocyanate, polypropylene glycol having a molecular weight of from about 2,000 to about 3,000 and glycerol monoricinoleate, said coated ammonium perchlorate being present in an amount between about 45 and about 95 percent by weight of said propellant composition and said resin binder being present in an amount between about 55 and about 5 percent by weight of said propellant composition.

12. A solid propellant composition which comprises a cured intimate mixture of finely divided aluminum, ammonium perchlorate having a surface coating adherent thereto, said surface coating having been obtained by treatment of said ammonium perchlorate with vinyl trichlorosilane; and a resin binder which comprises the reaction product of 2,4-tolylene diisocyanate, polypropylene glycol having a molecular weight from about 2,000 to about 3,000, and glycerol monoricinoleate; said aluminum being present in an amount not greater than about 40 percent by weight, said resin binder being present in an amount between about 40 and about 10 percent by weight, and said coated ammonium perchlorate being present in an amount between about 85 and about 40 percent by weight, all percentages being given on a total propellant weight basis.

13. The solid propellant composition of claim 12 wherein said 2,4-tolylene diisocyanate is present in stoichiometric excess over the amounts of polypropylene glycol and glycerol monoricinoleate initially present.

14. The solid propellant composition of claim 12 wherein said aluminum is present in an amount not greater than about 26 percent by weight of said propellant composition.

15. The method of preparing a solid propellant composition which comprises intimately dispersing a solid inorganic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an organo-silicon

material selected from the group consisting of compounds having the general formula



and mixtures thereof, wherein R is a radical selected from the group consisting of alkyl, aryl, and alkenyl radicals; X is a radical selected from the group consisting of halogen and alkoxy radicals; X' is a radical selected from the group consisting of halogen and alkoxy radicals; and Z is a radical selected from the group consisting of alkyl, aryl, alkenyl, halogen, and alkoxy radicals, in a resin binder and curing the mixture.

16. The method of preparing a solid propellant composition which comprises intimately dispersing a solid inorganic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an organo-silicon material selected from the group consisting of compounds having the general formula



and mixtures thereof, wherein R is a radical selected from the group consisting of alkyl, aryl, and alkenyl radicals; X is a radical selected from the group consisting of halogen and alkoxy radicals; X' is a radical selected from the group consisting of halogen and alkoxy radicals; and Z is a radical selected from the group consisting of alkyl, aryl, alkenyl, halogen, and alkoxy radicals, and aluminum in a resin binder and curing the mixture.

17. The method of preparing a solid propellant composition which comprises intimately dispersing a solid inorganic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with an organo-silicon material selected from the group consisting of compounds having the general formula



and mixtures thereof, wherein R is a radical selected from the group consisting of alkyl, aryl, and alkenyl radicals; X is a radical selected from the group consisting of halogen and alkoxy radicals; X' is a radical selected from the group consisting of halogen and alkoxy radicals; and Z is a radical selected from the group consisting of alkyl, aryl, alkenyl, halogen, and alkoxy radicals, in a binder mixture comprising a compound having two active hydrogen groups capable of reacting with an isocyanate selected from the group consisting of:

- (a) alkane diols having a chain length of from 2 to 20 carbon atoms, inclusive;
- (b) alkane dithiols having a chain length of from 2 to 20 carbon atoms;
- (c) alkene diols;
- (d) alkene dithiols;
- (e) cycloalkylene diols;
- (f) cycloalkylene dithiols;
- (g) aromatic diols;
- (h) aromatic dithiols;
- (i) dihydroxy polyesters having a molecular weight from about 1000 to about 2500;

(j) polyalkylene ether glycols having a molecular weight from about 400 to about 10,000;

(k) polysulfides with glycol end groups; and mixtures thereof;

5 a compound selected from the group consisting of:

- (1) alkane diisocyanates;
- (2) alkane diisothiocyanates;
- (3) alkene diisocyanates;
- (4) alkene diisothiocyanates;
- (5) alkylidene diisocyanates;
- (6) alkylidene diisothiocyanates;
- (7) cycloalkylene diisocyanates;
- (8) cycloalkylene diisothiocyanates;
- (9) cycloalkylidene diisocyanates;
- (10) cycloalkylidene diisothiocyanates;
- (11) aromatic diisocyanates;
- (12) aromatic diisothiocyanates;

and mixtures thereof;

20 and, as a cross-linking agent, a compound having not less than 3 groups polymerizable with a group selected from the class consisting of hydroxy, thiol, isocyanate, and isothiocyanate groups; and curing the mixture.

18. The method of preparing a solid propellant composition which comprises intimately dispersing a solid inorganic oxidizing salt having a surface coating adherent thereto, said surface coating having been obtained by treatment of said oxidizing salt with vinyl trichlorosilane, in a binder mixture comprising an aromatic diisocyanate, a polyether having a molecular weight of from about 400 to about 10,000, and a trihydroxy cross-linker compound; said coated inorganic oxidizing salt being present in an amount between about 45 and about 95 percent by weight of said propellant composition, said resin binder being present in an amount between about 55 and about 5 percent by weight of said propellant composition, and said aromatic diisocyanate being present in a stoichiometric excess over the amounts of said polyether and said trihydroxy cross-linker compound initially present, and curing the mixture.

19. The method of claim 18 wherein said solid inorganic oxidizing salt is ammonium perchlorate.

20. The method of preparing a solid propellant composition which comprises intimately dispersing ammonium perchlorate having a surface coating adherent thereto, said surface coating having been obtained by treatment of said ammonium perchlorate with vinyl trichlorosilane, and finely divided aluminum in a binder mixture comprising an aromatic diisocyanate, a polyether having a molecular weight of from about 400 to about 10,000, and a trihydroxy cross-linker compound and curing the mixture; said coated ammonium perchlorate being present in an amount between about 85 and about 40 percent by weight of said propellant composition, said aluminum being present in an amount not greater than about 40 percent by weight of said propellant composition, said binder mixture being present in an amount between about 40 and about 10 percent by weight of said propellant composition, and said aromatic diisocyanate being present in a stoichiometric excess over the amounts of said polyether and said trihydroxy cross-linker compound initially present.

No references cited.

65 BENJAMIN R. PADGETT, *Primary Examiner*.
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