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POLYURETHANE-BASE PROPELLANTS CONTAINING UNSATURATED HYDROCARBONS

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This invention relates to a method for greatly improving the aging stability of polyurethane propellants containing inorganic nitrate oxidizers and the resulting polyurethane-nitrate propellants of improved aging stability.

There is a practical advantage in using inorganic nitrates such as, for example, ammonium, alkali metal, and alkaline earth metal nitrates as oxidizer salts in polyurethane propellants since these materials are cheap and readily available. Furthermore, it is advantageous to employ inorganic nitrates as oxidizers since this permits the making of propellants having low burning rates such as burning rates in the neighborhood of 0.03 inch per second. Low burning rates are of paramount importance in many instances. For example, such propellants are particularly useful as gas generators.

In spite of their advantages as oxidizers in solid propellants, inorganic nitrate salts or mixtures of such nitrate salts with other oxidizer salts are known to impart poor aging stability to polyurethane propellants in which they are incorporated. Even when polyurethane-nitrate propellants are stored at room temperature they have a strong tendency to deteriorate by becoming tenderized and losing their elastomeric properties. If stored long enough such propellant eventually becomes either a semi-fluid paste or it changes to a brittle, nonelastic and easily pulverizable material. At elevated temperatures of storage polyurethane-nitrate propellants rarely, if ever, withstand aging for a period longer than about eight weeks. When stored at about 180° F. such propellants normally show marked degradation after only three days of aging.

It is therefore an object of this invention to prepare storage-stable polyurethane propellants containing nitrate oxidizers. It is another object of this invention to prepare storage-stable propellants having low burning rates. These and other objects of my invention will become apparent from the following detailed description.

I have found, and this is the essence of my invention, that when relatively small amounts of unsaturated hydrocarbons within the class and having the properties described below are incorporated in the polyurethane-nitrate propellants of this invention, the aging stability of the resulting propellants is remarkably enhanced. While I am not completely certain of the reason why unsaturated hydrocarbons of the type disclosed herein bring about such a pronounced improvement in the aging stability of polyurethane-nitrate propellants, I have found that without such a material present the inorganic nitrate decomposes and this decomposition is promoted by the trivalent nitrogen atom always present in the urethane linkage. It seems probable that this trivalent nitrogen atom takes over nitrate ($-\text{ONO}_2$) and partly takes over nitro ($-\text{NO}_2$) groups from the nitrate salt and that this subsequently breaks up the urethane linkage. These reactions are accelerated by temperatures above 100° F. and proceed quite rapidly at temperatures higher than about 150° F. I have further found that the rate of reaction between the nitrate salt and the polyurethane binder is proportionate to the over-all surface of the oxidizer dispersed in the binder. For example, a propellant contain-

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ing a nitrate salt whose average particle size is 150 microns deteriorates on aging faster than the same type of propellant containing the same nitrate salt but ground to a coarser particle size of only 300 microns average particle size.

While not bound by any theory, it is believed that the unsaturated hydrocarbon of the type employed in this invention prevents the nitrate oxidizer from reacting with nitrogen in the urethane linkage of the binder by forming on the oxidizer surfaces an adherent complex due to the surface affinity to the oxidizer. In accordance with this invention certain unsaturated hydrocarbons having more than one unsaturated carbon-to-carbon linkage in each molecule provide the desired surface complex for inorganic nitrates which, in order to secure complete inactivation of the nitrate salt oxidizer, at least one monomolecular film on the surface of each nitrate salt oxidizer particle must be provided. For ammonium nitrate salts, for example, having an average size of 100 microns or more (it is sufficient to use for each 100 weight parts of the oxidizer, 0.5 weight part of the unsaturated hydrocarbon). For the same nitrate salt oxidizer with an average particle size of 40 microns, the required minimum amount of the same type of unsaturated hydrocarbon should be fourfold or 2.0 weight parts.

The unsaturated hydrocarbon, in addition to improving the aging stability, also serves as a plasticizer for the propellant. Thus, the unsaturated hydrocarbon may be used as a partial or complete replacement for conventional propellant plasticizers such as dioctyl azelate, dioctyl phthalate, and monoisopropyl diphenyl.

The class of unsaturated hydrocarbons fulfilling the above requirements and suitable for purpose of this invention are those unsaturated aliphatic, acyclic hydrocarbon isoprenoids and terpenoids having a molecular weight of about 200 or above up to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit. In general, these compounds contain no more than two carbon-to-carbon unsaturated linkages for each 100 molecular weight unit.

In addition to the above-mentioned properties, the unsaturated hydrocarbons of this invention preferably also have the following characteristics. They have a freezing point below about -60°F . and preferably below -75°F . The unsaturated hydrocarbon should also preferably have a relatively low volatility at temperatures up to about 200° F. so that they will not evaporate to any extent from the composite propellant at these temperatures. Finally, the unsaturated hydrocarbon should be compatible with the polyisocyanate as well as with the reactive polymer and remain compatible with the produced in situ urethane elastomeric binder. At the same time, it must have a good wettability for the nitrate salt, enabling it to stick to the surface of the nitrate propellant during the mixing and curing process.

Within this class, as I have found, belong the group of terpenoids as well as isoprenoids, the lowest member of which is digeranyl ($\text{C}_{20}\text{H}_{34}$), M.W.=274, which contains four unsaturated carbon-to-carbon linkages per molecule. Another hydrocarbon very useful for the claimed purpose is squalene which has a molecular weight of 410, and has the chemical name 2,6,10,14,18,22-hexamethyltetracosahexene - 2,6,10,14,18,22. It contains six double-bonds per molecule. Next is lycopersen ($\text{C}_{40}\text{H}_{60}$), M.W.=546, containing eight double-bonds per molecule. From those three mentioned unsaturated hydrocarbons, the best are: lycopersen, which can be made synthetically from geranyl-bromide, and squalene which is an abundant by-product of the manufacturing of fish oils, in particular, shark liver oil. Both are low viscous liquids combining

a low freezing point with low volatility. In particular, squalene has the following desirable properties: Pour point -60°C ., boiling point -225 – -228°C ., 1 millimeter Hg; specific gravity at 20°C . from .858–.860; iodine No. from 360–370.

I have found that squalene has a very high wetting ability for all nitrate salts, but in particular for ammonium nitrate. With ammonium nitrate, squalene produces stable surface complexes which are characterized by being insoluble in hexane, with which otherwise squalene is miscible in all proportions.

Two equally effective methods of using the described unsaturated hydrocarbons with the nitrate salts have been developed.

One method consists in pretreating the nitrate salt or a nitrate salt mixture with the unsaturated hydrocarbon at temperatures from 60°F . to 300°F .; preferably at 180°F . for one to ten hours, preferably for five hours using for each 100 weight parts of the nitrate oxidizer from 0.2–5.0 weight parts; preferably 2 weight parts of the described unsaturated hydrocarbon. The thus stabilized nitrate salt can then be used as such in making the polyurethane-nitrate propellant.

Another method is to incorporate the described unsaturated hydrocarbon directly into the propellant formulation using amounts from 0.2–5.0 weight parts, preferably 2 weight parts per 100 weight parts of the nitrate salt, and proceed with the preparation of the propellant as usual.

My 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 copending patent application Serial No. 306,030, filed August 23, 1952. 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 my novel solid propellants are employed are ordinarily of the conventional type having one end open and leading into a venturi rocket nozzle.

The polyurethane binders of my invention are prepared by reacting a compound having two or more active hydrogen 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. These binders are more fully disclosed in assignee's copending U.S. patent applications, Serial Nos. 829,180 and 829,182, both filed on July 20, 1959.

It will be apparent that, where there are more than two active hydrogen, isocyanate, or isothiocyanate groups present in 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.

Where bifunctional reactants, such as dihydroxy compounds and diisocyanates, are employed to produce the polyurethane binders, a supplemental "cross-linking" agent can be employed, if desired, to provide a cross-linked resin binder. Compounds suitable as cross-linked agents for the polyurethane binders are those organic compounds having as the sole reacting groups three or more groups polymerizable with hydroxy or isocyanate groups.

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 the polyurethane binders are preferably diisocyanates but not necessarily so since, as explained above, other polyisocyanate (such as triisocyanates) or polyisothiocyanates may be employed if desired.

The preferred diisocyanate compounds are those having the formula $\text{NCO}-\text{A}-\text{NCO}$, wherein A is a saturated or unsaturated; open or closed chain, divalent organic radical. The group A may be entirely hydrocarbon or may be substituted by groups substantially unreactive with isocyanate or hydroxyl groups such as, for example, ketone, halogen, ester, sulfide, or ether groups. The group A normally contains from 1 to about 20 carbon atoms. The diisocyanate compounds particularly suitable as reactants for the preparation of polyurethane binders are alkane diisocyanates, such as: ethylene diisocyanate, trimethylene diisocyanate, and decamethylene diisocyanate; the alkene diisocyanates, such as: 1-propylene-1,2-diisocyanate, and 1-butylene-1,3-diisocyanate; the alkylidene diisocyanate, such as: ethylene diisocyanate, and propyldiene-1,1-diisocyanate; and the aromatic diisocyanates, such as: m-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, and 4,4'-diphenylmethane diisocyanate.

The preferred hydroxy starting materials for the 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. Dihydroxy compounds particularly suitable as reactants for the polyurethane binders of this invention include alkene diols having a chain length of from 2 to 20 carbon atoms inclusive, such as 2,2-dimethyl-1,3-propendiol, ethylene glycol, and aromatic diols such as catechol, resorcinol, and 2,4-toluenediol.

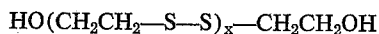
Other dihydroxy compounds suitable for the polyurethane reaction of this invention are polyesters such as those obtained from the reaction of a dihydric alcohol such as ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, or hexamethylene glycol with a dicarboxylic acid such as succinic acid, adipic acid, sebacic acid, oxadibutyric acid, sulfodipropionic acid, and related compounds. The polyesters most suitable for purpose 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 above-mentioned polyesters can be prepared from either saturated or unsaturated dihydric alcohols and saturated or unsaturated dicarboxylic acids. The anhydrides of these acids are suitable in the preparation of polyesters for the polyurethane reaction of my invention. The usual and preferred manner of making suitable polyesters is to react a mixture of a saturated dicarboxylic acid (such as adipic acid, sebacic acid, or the like) or anhydride and an unsaturated or aromatic dicarboxylic acid or anhydride with a dihydric alcohol.

In addition to the polyesters, polyalkylene ether polyols such as polyethylene ether glycols, polypropylene ether glycols, and copolymers of ethylene oxide and propylene oxide, or the polyalkylene ether polyol adduct obtained by the addition of ethylene oxide, propylene oxide, or mixtures thereof to 1,2,6-hexanetriol, pentaerythritol, trimethylol propane, or glycerine. Normally, the polyalkylene ether polyols of this invention have two or three

hydroxy groups per molecule and have a molecular weight of from about 400 to about 10,000.

Polysulfides having two or more thiol groups, such as those having the general formula,



where x is a whole number, are other suitable binder ingredients for use in my invention

It is well-known to those skilled in the art that polyisothiocyanates and polythiol compounds react to yield urethane-type products as do the polyisocyanate 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.

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.

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 are particularly suitable as cross-linking agents are glycerol monoricinoleate; glycerol triricinoleate; 1,2,6-hexanetriol; methylene bis-(orthochloroaniline); monohydroxyethyl trihydroxypropyl ethylenediamine; polyaryl polyisocyanates; N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylenediamine; triethanolamine; trimethylolpropane; and triisocyanates, such as toluene-2,4,6-triisocyanate. Preferably, the cross-linking agent contains three or four hydroxy groups per molecule and have a molecular weight of from about 80 to about 1000.

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

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

The oxidizers employed in the propellants of this invention are as noted above, the ammonium, alkali metal and alkaline earth metal nitrates. However, these nitrates can be used in mixtures with other oxidizers known to those skilled in the art. Normally, the nitrate oxidizer accounts for at least 10 percent by weight of the total oxidizer mixture. Examples of suitable oxidizing salts are the chromates, dichromates, permanganates, chlorates, and perchlorates of the alkali or alkaline earth metals (such as potassium, sodium, or calcium); ammonia; hydrazine; or guanidine. Nitronium perchlorate may also be used. When another oxidizer is used with the nitrate oxidizer the preferred mixture is a mixture of ammonium nitrate and ammonium perchlorate.

Various additives may be employed in preparing the polyurethane binders of this invention. For example, plasticizers familiar to those skilled in the art, such as dioctyl phthalate, dioctyl azelate; etc., may be utilized.

It should be understood, as noted above, that the unsaturated hydrocarbon stabilizers themselves aid in plasticization, and thus may be useful wholly or in part in lieu of the conventional polyurethane plasticizers. Also, catalysts for the polyurethane reaction such as triethylamine and other tertiary amines, ferric acetylacetonate and other metal acetylacetonates such as vanadyl acetylacetonate, boron trifluoride, etc., can be employed if desired. The catalysts can be employed in quantities within

the range from mere traces up to amounts equivalent to about one percent by weight of the total mass, and even higher. Normally, amounts of from about 0.02 to about 0.10 percent by weight basis are employed.

Burning rate modifiers and other additives such as anti-oxidants, wetting agents, methal fuels, anti-foaming agents, etc., can be employed, if desired, in the formulation of my novel propellants. In this connection, copper chromite when utilized in small quantities preferably not greater than about 1 percent (and for best results not greater than about 0.5 percent, of the total propellant weight) is useful for increasing the burning rate of the propellant. Certain well-known agents, such as lecithin, are known to be useful processing aids in the preparation of my novel propellants. A particularly suitable wetting agent is a mixture of sorbitan monooleate and polyoxyethylene esters of mixed fatty and resin acids. For best results, the wetting agents should be employed in proportions comprising not more than about 1 percent by weight of the total propellant composition and preferably in proportions much lower than this. There can also be added to the propellant of this invention from about 0.5 to about 20 percent by weight of total propellant of metal fuels such as powdered aluminum and powdered beryllium. Various additives other than those mentioned can be employed, in minor amounts, within the scope of this invention.

In preparing the novel 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.

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 the reaction rate is sufficiently rapid for economical production and yet the temperature is not so high as to produce shrinkage and internal stresses which must be avoided at all costs, especially in the case of large solid propellant motors.

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 have found to be particularly effective for mixing my propellant ingredient, 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.

There are many ways of processing the various ingredients within the scope of this invention in the formulation of propellants therefrom. 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 or at the same time as the addition of the diisocyanate or subsequent to this addition. The various additives do not all have to be added at the same stage of processing and, in fact, it has been found preferable in most cases to deviate from this procedure. One technique which is quite satisfactory (where the major ingredients and order of addition of these ingredients are as described above) comprises addition of the wetting agent or agents, along with the plasticizer, to the diol and cross-linker in the mixer; addition of the burning rate modifiers during addition of the inorganic oxidizer; and addition of the curing catalyst 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, for processing the major components in the preparation

for processing the major components in the preparation of my novel propellants. For example, the diol can first be mixed with the oxidizer, after which the diisocyanate can be added, along with the catalyst and cross-linker.

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° F. to about 180°. As pointed out above, the propellant mixture can be cast directly into a rocket chamber lined with an inert liner material, and polymerized (cured) therein if this procedure appears to be desirable.

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 the novel solid propellants of my invention. The amount of binder is preferably employed in an amount within the range from about 55 to about 5 percent by weight of the propellant. The unsaturated hydrocarbons of this invention are usually present in amounts from about 0.05 to about 10 percent by weight based on the total weight of propellant.

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 my novel solid propellants, improved mechanical properties are obtained if a slight excess of isocyanate groups over hydroxy groups is present in the fuel mixture. Consequently, for the best results 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 therein.

The various additives and minor components of the novel propellants normally comprise a very small percentage of the total propellant weight. Thus, they will usually be present in combined amounts not greater than that corresponding to about 10 percent (and preferably about 4 or 5 percent) of the total propellant weight.

The following examples are included for the purpose of illustrating the novel process and propellant compositions of my invention. Applicant wishes to emphasize that these examples are intended for illustrative purposes only and that they should not be construed as limitative of the scope of the invention to the particular conditions and proportions set forth therein.

In the examples, the parts are by weight unless otherwise indicated.

Example I

This example describes a particular method of preparing a novel propellant composition according to this invention from the following ingredients.

Ingredient:	Weight percent
Ammonium nitrate	80.00
Polypropylene glycol (mol. wt. 1800-1900) ..	12.22
2,4-tolylene diisocyanate	2.02
Glycerol monoricinoleate	1.63
Squalene	2.84
Lecithin	0.14
Phenyl dibetanaphthylamine	0.12
Ferric acetylacetonate	0.03
Copper chromite	1.00

Prior to the actual mixing of the polyurethane propellant, the major constituents of the fuel system, tolylene diisocyanate and polypropylene glycol, are "degassed" by heating to an elevated temperature to remove residual moisture, carbon dioxide, and undesired monomeric material. The residual moisture, carbon dioxide, and undesired monomeric materials are vented to the atmosphere. The heating is accomplished under vacuum for a specified period sufficient to yield materials of an established minimum purity. The oxidizer is dried and ground

at an elevated temperature and added to the mixture while hot.

A conventional mixer equipped with facilities for heating, cooling, and vacuumising the propellant batch is used in the mixing operation. Heating of the mixer is begun and the polypropylene glycol and glycerol monoricinoleate are charged to the mixer. The lecithin is mixed with the squalene until homogeneous and this solution is then added to the mixer. These components are mixed until homogeneous and the oxidizer addition is begun. During this addition, the copper chromite is also added. When all the oxidizer and additives have been added, the mixer is sealed and vacuumized and the batch is mixed at 150° F. to 180° F. for one hour.

At the completion of the heating period, the batch is cooled as rapidly as possible to 65° F. while continuing to mix under vacuum. During this cooling period the tolylene diisocyanate and ferric acetyl acetate (FeAA) are stirred together until the FeAA is completely in solution. When the desired temperature has been attained, this solution is added to the batch and mixing is continued for 15 minutes under vacuum. The mixer is then stopped, vacuum released and the batch is cast and cured at 130° F. The cured propellant obtained retained its stability after many months of storage.

Example II

A mixture containing 22 parts of ammonium nitrate, 5 parts lithium nitrate and 15 parts of sodium nitrate making together 42 parts of the nitrate salt oxidizer was ground in the presence of 2.0 parts of squalene at a temperature of 180° F. to an average particle size of 250 microns. This procedure required five hours after which the resultant tan colored powder was cooled and used in a propellant formulation, the composition of which was as follows:

Ingredient	Weight Percent	
	Treated Propellant A	Control Propellant B
Nitrate salt mixture prepared as above	44.00	44.00
Nitrate salt mixture as above, non-treated	36.00	36.00
Potassium perchlorate	12.22	12.22
Polypropylene glycol	1.63	1.63
Glycerol monoricinoleate	2.02	2.02
2,4-tolylene diisocyanate	1.00	1.00
Copper chromite	0.16	0.16
Phenyl dibetanaphthylamine	0.14	0.14
Lecithin	0.13	0.13
Ferric acetylacetonate	1.00	1.00
Diocetyl phthalate		

After curing, both propellants were tested in an Instron apparatus for tensile strength and elongation at +60° F. and placed in an aging oven for twelve weeks at a temperature of +180° F. After aging for three weeks they were again tested for tensile strength and elongation with the following results:

Before Aging	Propellant A	Propellant B
Tensile strength at maximum stress at +60° F., p.s.i.	61.5	73.2
Elongation at maximum stress at +60° F., percent	22.1	20.8
After Aging	Propellant 4	Propellant 5
Tensile strength at maximum stress at +60° F.	74.2 p.s.i.	Decomposed.
Elongation at maximum stress at +60° F.	70.2%	Do.

As is seen also from Example No. II only propellant No. A in which the nitrate salt mixture was pretreated with squalene withstood aging while propellant No. B

containing the same, but untreated, nitrate salt mixture decomposed after 3 weeks of aging.

Example III

Three propellants were made containing, as oxidizer, a mixture of ammonium and potassium nitrate mixed with ammonium perchlorate. Propellants No. D and E contained dioctyl phthalate and mono-isopropyl diphenyl, respectively, instead of lycopersen as the plasticizer. Otherwise, their composition and method of manufacturing were the same.

Ingredient	Weight Percent		
	Propellant C	Propellant D	Propellant E
Ammonium nitrate average particle size 300 microns	50.00	50.00	50.00
Potassium nitrate average particle size 300 microns	10.00	10.00	10.00
Ammonium perchlorate	20.00	20.00	20.00
Copper Chromite	1.00	1.00	1.00
Lecithin	0.14	0.14	0.14
Phenyl dibetanaphthylamine	0.10	0.10	0.10
Ferric acetylacetonate	0.03	0.03	0.03
Polypropylene glycol	12.22	12.22	12.22
Glycerol Monoricinoleate	1.63	1.63	1.63
2,4-tolylene diisocyanate	2.02	2.02	2.02
Lycopersen	2.84		
Dioctyl phthalate		2.84	
Monisopropyl diphenyl			2.84

These propellants were tested and aged as described in Example II.

Before Aging	Propellant C	Propellant D	Propellant E
Tensile strength at maximum stress at 60° F., p.s.i.	38.2	64.7	63.0
Elongation at maximum stress at 60° F., percent	14.0	15.8	10.2

After Aging for 12 Weeks at 180° F.	Propellant C	Propellant D	Propellant E
Tensile strength at maximum stress at 60° F.	68.0 p.s.i.	Decomposed to fluid paste.	Decomposed to fluid paste.
Elongation at maximum stress at 60° F.	9.2%	do.	Do.

As it is seen from Example III, lycopersen, when used in polyurethane propellant C, provides good protection against aging by stabilizing the propellant for a long period of storage. Example III illustrates the undesirable aging properties of propellants D and E containing known plasticizers. These two propellants deteriorated within twelve weeks to such an extent as to no longer be useful for their intended purpose.

The following are additional propellants which were prepared according to my invention and found to possess excellent aging stability.

Example IV

Ingredient:	Weight percent
Ammonium perchlorate	55.16
Ammonium nitrate	23.64
Copper chromite	1.00
Lecithin	0.14
Phenyl dibetanaphthylamine	0.20
Ferric acetylacetonate	0.03
Polypropylene glycol	12.22
Glycerol monoricinoleate	1.63
Squalene	3.96
Toluene diisocyanate	2.02

Example V

Ingredient:	Weight percent
Ammonium nitrate	78.80
Copper chromite	1.00
Lecithin	0.14
Phenyl dibetanaphthylamine	0.20
Ferric acetylacetonate	0.03
Polypropylene glycol	2.22
Glycerol triricinoleate	1.63
Squalene	3.96
Hexamethylene diisocyanate	2.02

Having fully described my invention, it is intended that it be limited only by the lawful scope of the appended claims including a reasonable range of equivalents.

I claim:

1. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a polyurethane 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 Zerewitinoff method and capable of 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 hydroxy groups; and an unsaturated aliphatic, acyclic hydrocarbon selected from the group consisting of isoprenoids and terpenoids and having a molecular weight of from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit, said solid inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and said unsaturated hydrocarbon compound being present in an amount between about 0.05 and about 10 percent by weight of the propellant composition.

2. The solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of ammonium nitrate, a polyurethane resin binder which comprises the reaction product of the compound having as its sole reacting groups not less than two active hydrogen groups as determined by the Zerewitinoff method and capable of polymerizing with an isocyanate, and a stoichiometric excess of a compound having as its sole reacting groups 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; and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight of from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit, said ammonium nitrate being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and said unsaturated hydrocarbon compound being present in an amount between about 0.05 and about 10 percent by weight of the propellant composition.

3. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a polyurethane binder which comprises the reaction product of a polyalkylene ether polyol having from 2 to 3 hydroxy groups per molecule, and an organic diisocyanate capable of undergoing a urethane-type reaction with said polyol, and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight of from about

200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit; said inorganic oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and said unsaturated hydrocarbon compound being present in an amount between about 0.05 and about 10 percent by weight of the propellant composition.

4. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a polyurethane 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 and capable of 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 hydroxy groups, and squalene, said inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and the squalene being present in an amount between 0.05 and about 10 percent by weight of the propellant composition.

5. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a cross-linked polyurethane resin binder which comprises the reaction product of a polyalkylene ether glycol, a cross-linking compound containing from three to about four hydroxy groups per molecule and having a molecular weight of from about 80 to about 1000, and a stoichiometric excess of an organic diisocyanate, the stoichiometric excess being calculated as an excess over all active hydrogen groups capable of polymerizing with an isocyanate initially present in said glycol and said cross-linking agent, and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight of from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit; said solid inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said cross-linked polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and said unsaturated hydrocarbon compound being present in an amount from about 0.05 to about 10 percent by weight of the propellant composition.

6. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a cross-linked polyurethane resin binder which comprises the reaction product of a dihydroxy polyester having a molecular weight of about 1000 to about 2500, a cross-linking compound containing from 3 to 4 hydroxy groups per molecule and having a molecular weight of from about 80 to about 1000, and a stoichiometric excess of an organic diisocyanate, the stoichiometric excess being calculated as an excess over all active hydrogen groups capable of polymerizing with isocyanate initially present in said polyester and cross-linking compound, and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight of from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 1000 molecular weight unit; said solid inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said cross-linked

polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and said unsaturated hydrocarbon compound being present in an amount between about 0.05 and about 10 percent by weight of the propellant composition.

7. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a polyurethane resin binder which comprises the reaction product of an aromatic diisocyanate, a polyalkylene ether glycol having a molecular weight from about 400 to about 1000, and a trihydroxy cross-linker compound; and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit; the inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, the polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition and the unsaturated hydrocarbon compound being present in an amount between about 0.05 and about 10 percent by weight of the propellant composition.

8. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, and a polyurethane resin binder which comprises the reaction product of an aromatic diisocyanate, a polyalkylene ether glycol having a molecular weight from about 400 to about 1000, and a trihydroxy cross-linker compound, the aromatic diisocyanate being present in stoichiometric excess, the stoichiometric excess having been calculated as an excess over the total amount of polyalkylene ether glycol and trihydroxy compounds initially present; and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit; the inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, the polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and the unsaturated hydrocarbon compound being present in an amount from about 0.05 and about 10 percent by weight of the propellant composition.

9. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a cross-linked polyurethane resin binder which comprises the reaction product of an aromatic diisocyanate, a polyalkylene ether glycol having a molecular weight from about 400 to about 1000, and glycerol monoricinoleate; and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit, the inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, the cross-linked polyurethane resin binder being present in an amount between about 55 and about 5 percent by weight of the propellant composition, and the unsaturated hydrocarbon compound being present in an amount between about 0.05 and about 10 percent by weight of the propellant composition.

10. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic nitrate oxidizing salt, a polyurethane binder which comprises the reaction product of 2,4-tolylene diisocyanate, polypropylene glycol having a molecu-

lar weight of from about 400 to about 10,000 and glycerol monoricinoleate; and unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit; the inorganic nitrate oxidizing salt being present in an amount between about 45 and about 95 percent by weight of the propellant composition, the polyurethane resin being present in an amount between about 55 to about 5 percent by weight of the propellant composition, and the unsaturated hydrocarbon compound being present in an amount between 0.05 and 10 percent by weight of the propellant composition.

11. A solid propellant composition which possesses improved aging stability which comprises a cured intimate mixture of a solid inorganic oxidizing salt, at least 10 percent by weight of said solid inorganic oxidizing salt being a solid inorganic nitrate oxidizing salt, a polyurethane 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 Zerewitinoff method and capable of 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 hydroxy groups, and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for every 100 molecular weight unit; the total amount of said solid inorganic oxidizing salts being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said polyurethane resin binder being present in an amount between about 55 and 5 percent by weight of the propellant composition, and said unsaturated hydrocarbon compound being present between about 0.05 and about 10 percent by weight of the propellant composition.

12. A solid propellant composition possessing improved aging stability which comprises a cured intimate mixture of a solid inorganic oxidizing salt mixture consisting essentially of ammonium nitrate and ammonium perchlorate, said ammonium nitrate accounting for at least 10 percent by weight of said oxidizing salt mixture, a polyurethane 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 Zerewitinoff method and capable of 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 hydroxy groups; and an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit; the said mixture of ammonium nitrate and ammonium perchlorate being present in an amount between about 45 and about 95 percent by weight of the propellant composition, said polyurethane resin binder being present in an amount between about 55 and 5 percent by weight of the propellant composition and said unsaturated hydrocarbon compound being present in an amount between 0.05 and about 10 percent by weight of the propellant composition.

13. The solid propellant composition of claim 12 in which there is intimately dispersed an amount not greater than about 2 percent by weight of the propellant composition, of a burning rate accelerator.

14. The solid propellant of claim 12 in which there is intimately dispersed an amount of copper chromite not

greater than about 2 percent by weight of the propellant composition, as a burning rate accelerator.

15. The method of preparing a solid propellant composition possessing improved aging stability which comprises intimately dispersing from about 45 to about 95 percent by weight of a solid inorganic nitrate oxidizing salt, and from about 0.05 to about 10 percent by weight of an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit, in from about 5 percent to about 55 percent by weight of a polyurethane binder mixture comprising a compound having at least two active hydrogen groups as determined by the Zerewitinoff method and capable of reacting with an isocyanate, and a stoichiometric excess of a compound having as its sole reacting groups not less than two groups capable of undergoing a urethane-type reaction with hydroxy groups, the said excess being calculated as an excess over all active hydrogen groups capable of polymerizing with an isocyanate initially present.

16. The method of preparing a solid propellant composition possessing aging stability which comprises intimately dispersing from about 45 to about 95 percent by weight of a solid inorganic oxidizing salt mixture, at least 10 percent by weight of said mixture being a solid inorganic nitrate oxidizing salt, and from about 0.05 to about 10 percent by weight of an unsaturated aliphatic, acyclic hydrocarbon compound selected from the group consisting of isoprenoids and terpenoids and having a molecular weight from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit; in from about 5 percent to about 55 percent by weight of a polyurethane binder mixture comprising a compound having at least two active hydrogen groups as determined by the Zerewitinoff method and capable of reacting with an isocyanate, and a stoichiometric excess of a compound having as its sole reacting groups not less than two groups capable of undergoing a urethane-type reaction with hydroxy groups, the stoichiometric excess being calculated as an excess over all active hydrogen groups capable of polymerizing with an isocyanate initially present.

17. The method of preparing a solid propellant composition possessing improved aging stability which comprises intimately dispersing from about 45 to about 95 percent by weight of a solid inorganic nitrate oxidizing salt containing a surface coating of an unsaturated aliphatic acyclic hydrocarbon selected from the group consisting of isoprenoids and terpenoids and having a molecular weight of from about 200 to about 1000 and having at least one carbon-to-carbon unsaturated linkage for each 100 molecular weight unit, the amount of said unsaturated hydrocarbon compound present on the nitrate salt being from about 0.2 to about 5.0 parts by weight per 100 parts by weight of the said nitrate salt; in from about 5 to about 55 percent by weight of a polyurethane binder mixture comprising a compound having at least two active hydrogen groups as determined by the Zerewitinoff method and capable of polymerizing with an isocyanate, and a stoichiometric excess of the compound having as its sole reacting groups not less than two groups capable of undergoing a urethane-type reaction with hydroxy groups, the stoichiometric excess being calculated as an excess over all active hydrogen groups capable of polymerizing with an isocyanate initially present.

No references cited.

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