

[54] **METHOD OF INCREASING PROPELLANT BURNING RATE BY THE USE OF HIGH CONDUCTIVE WIRES**

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[22] Filed: **Jan. 17, 1964**

[21] Appl. No.: **338,527**

[52] U.S. Cl. **149/5, 102/102, 149/19, 149/20, 149/21, 149/42**

[51] Int. Cl. **C06d 5/06**

[58] Field of Search **149/2, 5, 37-44, 149/21, 114, 19, 20; 102/98**

[56] **References Cited**

UNITED STATES PATENTS

3,109,374	11/1963	Rumbel et al.	149/2
3,147,161	9/1964	Afere et al.	149/19
3,163,113	12/1964	Davis et al.	102/102

Primary Examiner—Benjamin R. Padgett

EXEMPLARY CLAIM

4. A solid propellant composition which comprises a cured intimate mixture of a solid non-metallic oxidizing salt 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 capable of polymerizing with an isocyanate as determined by the Zerewitinoff method, 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 as a burning rate additive, elongated metallic staples having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec) (sq.cm.) (°C/cm) and a melting point above about 600°C, in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

17 Claims, No Drawings

METHOD OF INCREASING PROPELLANT BURNING RATE BY THE USE OF HIGH CONDUCTIVE WIRES

This invention pertains to a novel rapid burning solid propellant composition and to the method for its preparation.

Solid propellant rocket motors have been previously employed in tactical, intermediate range and intercontinental ballistic missiles. For these applications the propellant normally need only be of moderate burning rate since ample time is provided for the production of the necessary thrust. However, it has now become necessary to provide a solid propellant rocket motor for use in the interception of incoming ballistic missile nuclear warheads. To be successful, such an antimissile missile must be capable of rising very rapidly from the ground upon receiving directions from a computer and proceed to the point of interception which must be far enough from the ground so that the incoming warhead may be destroyed by nuclear explosives without endangering the underlying land mass. In order that this may be accomplished, the solid propellant employed in the antimissile missile must be capable of producing a large thrust very quickly. To provide this high acceleration, the propellant must possess a high burning rate.

It is therefore an object of this invention to prepare a novel propellant which possesses a sufficiently high burning rate to be suitable in an antimissile missile. Specifically, it is an object of this invention to prepare a solid rocket propellant which has a burning rate 300 to 500 percent of that obtainable with ordinary solid rocket propellants. These and other objects of this invention will be apparent from the detailed description which follows.

It has now been found that a solid propellant composition of high burning rate may be obtained by incorporating therein metallic staples in an effective amount, normally from about 1 percent to about 15 percent by weight of the total propellant composition. The staples of this invention are of long and narrow dimensions, that is, elongated. The staples may be of any cross-sectional shape but normally they are rectangular, square or circular in cross-section.

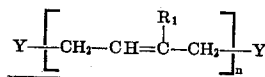
The metallic staples which are employed as burning rate additives in the propellants of this invention are comprised of any metals or metal alloys of high heat conductivity [from about 0.10 to about 1.05 gram-cal./(sec.)(sq.cm.)(°C/cm.)] and high melting point (above about 600°C) such as copper, aluminum, iron, stainless steel, hafnium, brass, zirconium, copper-aluminum alloy, aluminum coated nickel, nickel coated aluminum and palladium coated aluminum. These coated staples are prepared by electrolytic techniques known to those skilled in the art. When the metallic staples are circular in cross-section, they may vary in diameter from about 2.0 to about 10 mils, and in length from about 50 to about 500 mils. Preferably, such needle-like materials have a length of from about 250 mils to about 375 mils. The staples of my invention having a square cross-section preferably measure from about 0.5 to about 10 mils on a side and are from about 50 to about 500 mils in length. The staples of rectangular cross-section measure from 0.4 to about 5.0 mils on the short side and from about 1.0 to about 20 mils on the long side and are from about 50 to about 500 mils in length. These metallic staples may be incorporated into

the propellant any time during the processing operation prior to the casting and curing steps.

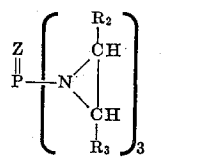
When the staples are used according to the practice of this invention, the burning rate is increased above that obtained by addition of known burning catalysts. Further, the staples of this invention provide increased burning rate without adversely affecting the specific impulse of the propellant. However, it is contemplated that where even higher burning rates are required, conventional burning rate catalysts such as copper chromite, in amounts from about 0.1 to about 2 percent by weight of total propellant, can be used in conjunction with the metallic staples.

As the primary propulsion source for an antimissile missile, propellants of this invention can be conveniently ignited by a conventional igniter, as for example, the igniter disclosed in Assignee's U.S. Pat. No. 3,000,312, issued Sept. 19, 1961. The rocket chambers in which the novel solid propellants are employed are ordinarily of a conventional type having one open end which leads to a venturi nozzle. Upon ignition, large volumes of gases are produced and exhausted through the nozzle to create thrust.

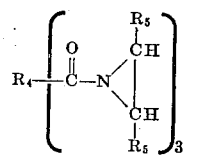
A preferred class of binders for use in the rapid burning propellants of the present invention are the reaction products of a carboxy-terminated polydiolefin of the formula:



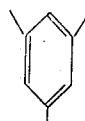
wherein R_1 is hydrogen or methyl, Y is a functional terminal group selected from the class consisting of carboxy, hydroxy, amine and mercapto; and n is an integer of from 8 to about 50; and an aziridinyl curing agent of one of the following types:



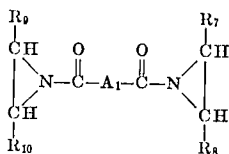
wherein Z is oxygen or sulfur; and R_2 and R_3 are hydrogen or lower alkyl such as methyl, ethyl and pentyl;



wherein R_4 is a trivalent organic radical of the formula:



and R_5 and R_6 is hydrogen or lower alkyl of from 1 to about 4 carbons; and



wherein A_1 is alkylene, preferably lower alkylene of from one to about 12 carbons, and R_7 , R_8 , R_9 and R_{10} are hydrogen or lower alkyl of from one to about four carbons. Normally, the aziridinyl curing agent is employed in an amount from 1 to about 40 parts per 100 parts of the functionally-terminated polydiolefin. The preferred polydiolefin of the above formula is polybutadiene or polyisoprene having a molecular weight of from about 400 to about 5,000, a viscosity at 77°F of from about 5 to about 500 poise, and is carboxy-terminated ($Y = COOH$).

Typical aziridinyl curing agents within the scope of the foregoing formulae include:
 tris(N -1',2'-butylene)trimesamide,
 tri(2-methyl-3- n -butyl-1-aziridinyl)phosphine oxide,
 tri(2-ethyl-3-octadecyl-1-aziridinyl)phosphine oxide,
 tri(2-methyl-3-cyclopentyl-1-aziridinyl)phosphine oxide,
 tri(2-methyl-3-benzyl-1-aziridinyl)phosphine oxide,
 tri(1-aziridinyl)phosphine sulfide,
 tri(2-methyl-1-aziridinyl)phosphine sulfide,
 tri(2-eicosyl-1-aziridinyl)phosphine sulfide, and
 tri(2-methyl-3-cyclohexyl-1-aziridinyl)phosphine sulfide.

The polyurethane binders which can be used in my propellants are prepared by reacting a compound having two or more active hydrogen containing groups capable of polymerizing with an isocyanate as determined by the Zerewitinoff method, with an organic compound having as the sole reacting groups, two or more isocyanate or isothiocyanate groups. The active hydrogen containing groups are preferably hydroxy or thiol.

It will be apparent that, where more than two active hydrogen, isocyanate, or isothiocyanate groups are present in any of the polyurethane reactants, the structure of the polyurethane binder will contain at least some cross-linking. 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 provide a product having a cross-linked structure. Compounds suitable as cross-linking agents for the polyurethane binders are those compounds having as the sole reacting groups at least three groups polymerizable with active hydrogen or isocyanate groups.

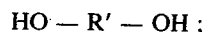
Examples of compounds which we have found to be particularly suitable as cross-linking agents are 1,2,6-hexanetriol; methylene bis-(*ortho*chloroaniline); monohydroxyethyl trihydroxypropyl ethylenediamine; N,N,N',N' -tetrakis (2-hydroxypropyl) ethylenediamine; triethanolamine; and trimethylolpropane.

A wide variety of polyurethane binders for the propellants of this invention can be prepared by varying the starting materials. These polyurethane binders are

disclosed in greater detail in Assignee's co-pending patent applications Ser. No. 829,180 and Ser. No. 829,182, both filed July 23, 1959.

The preferred diisocyanate compounds are saturated or unsaturated; aliphatic or aromatic; open or closed chain; and substituted or not by groups substantially unreactive with isocyanate or hydroxyl groups such as ketone or ether groups. Diisocyanate compounds such as tetramethylene diisocyanate, decamethylene diisocyanate; *m*-phenylene diisocyanate; diphenylene-4,4-diisocyanate; 2,4-tolylene diisocyanate; 3-nitroazobenzene-1,3-pentane diisocyanate; duren diisocyanate; and 2,6-tolylene diisocyanate are particularly suitable as reactants for the preparation of polyurethane binders.

The preferred hydroxy starting materials for the polyurethane binders are dihydroxy compounds having the general formula:



where R' is a divalent organic radical, such as alkylene or arylene. 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.

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, with a dicarboxylic acid such as succinic acid. The polyesters most suitable for purposes of this invention are those having a molecular weight from about 1,000 to about 2,500.

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.

Other binders which may be employed in my novel propellants include resinous binders such as rubbers, polysulfides, and rubber-polysulfide mixtures.

Examples of rubber binders which can be employed within the scope of this 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 polychloroprene. The polysulfides suitable as solid propellant binders are exemplified by 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 U.S. Pat. No. 3,012,866, issued Dec. 12, 1961.

Still other examples of polymeric organic material suitable as binders are phenol-aldehyde resins, polyester resins, acrylate resins and polyalkylene resins.

The so-called polyester resins suitable for use as propellant binders are formed by reacting a polyhydric alcohol with a polycarboxylic acid and copolymerizing therewith a monomeric ethylenically unsaturated compound, compatible with the resin. To permit heteropolymerization between the polyester and ethylenically unsaturated 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 compound-
ing the polyester resins are, for example, the aliphatic
dibasic acids, including oxalic, malonic, succinic, glu-
taric, adipic, pimelic, sebacic and azelic. The unsatu-
rated acids useful as the acidic components in forming
polyester resins are maleic acid, fumaric acid, citra-
conic acid and mesaconic acid, itaconic acid. The an-
hydrides such as itaconic anhydrides and phthalic an-
hydride may also be used to supply the desired unsatu-
ration.

Regardless of which of the saturated acids are used,
the degree of unsaturation necessary to provide cross-
linkage with the ethylenically unsaturated 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. For the polyhydric alcohol component any of the
following alcohols may be used: dihydric alcohols such
as ethylene glycol, diethylene glycol, triethylene glycol
and propylene glycol; a trihydric alcohol such as glycerol;
tetrahydric alcohols such as the erythritols and
pentaerythritols; pentitols which include arabitol,
adonitol and xylitol; hexatols including mannitol; sor-
bitol and dulcitol; heptitols such as persitol and volami-
tol; or mixtures of any of the above alcohols may be
also employed if desired.

The ethylenically unsaturated component of the
polyester resin binders may be styrene, vinyl acetate,
methyl methacrylate, allyl diglycol carbonate, diallyl
maleate, diallyl glycolate, propylene, butadiene, etc.; as
well as derivatives of any of the above substances which
are capable of polymerization with the polyester resin.

The polyester resins suitable as propellant binders
and their methods of preparation are more fully dis-
closed in Assignee's U.S. Pat. No. 3,031,288, issued
Apr. 24, 1962.

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

Other acrylate binders suitable for use in my inven-
tion are prepared by copolymerizing polymerizable
substances containing unreduced oxygen in the mole-
cule, such as the nitro and nitroether-substituted al-
kenoic acids and esters. Specific examples of nitro-
containing monomers which copolymerize to form acry-
late 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 oxy-
gen-containing monomers and any one or more of the
above-mentioned monomers containing unreduced oxy-
gen 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. Pat. application Ser. No. 321,941, filed
Nov. 21, 1952, and now abandoned.

Polyurethane resins containing unreduced oxygen
are suitable binders for the propellants of my 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.
Pat. application, Ser. No. 728,491, filed Apr. 14, 1958.

Illustrative of other solid propellant binders suitable
for use in the novel propellants of this invention are
those disclosed in U.S. Pat. No. 2,479,828 and British
Pat. No. 579,057.

Another class of binder materials useful in the prepa-
ration of the propellants of this invention are the low
molecular weight isoolefin-polyolefin copolymers of
the type disclosed in Assignee's copending U.S. Pat. ap-
plication Ser. No. 202,351, filed June 8, 1962.

Still other types of binders suitable for use in my
novel solid propellant composition are nitrocellulose-
plasticizer binders of the type prepared by curing mix-
tures of finely divided nitrocellulose and suitable plasti-
cizers such as pentaerythritol trinitrate. Binders of this
type and their methods of preparation are well-known to
those skilled in the propellant art.

A finely divided nitrocellulose suitable for use in the
preparation of the subject binders is obtained by first
dissolving nitrocellulose, preferably prepared from cot-
ton linters, in a solvent such as an ethyl acetate-
mixture, an ethyl acetate-ethanol mixture, or nitro-
methane to form a lacquer. The lacquer is slurried in
an aqueous medium containing a suspending agent
such as methyl cellulose in combination with an emulsi-
fier such as turkey red oil and an agent to prevent ag-
glomeration such as, for example, sodium chloride as
a result of which the nitrocellulose precipitates from
the solvent and is recovered as a particulate material
having an average particle size of 10 to 12 microns and
an over-all particle size range of from about 1 to about
35 microns. Finely divided nitrocellulose prepared by
the above-described method is known to those skilled
in the art as plastisol grade nitrocellulose and will be
hereinafter referred to as such. Plastisol grade nitrocel-
lulose is readily available on the open market.

The propellants of this invention contain, as oxidiz-
ers, oxidizing salts such as the chromates, dichromates,
permanganates, nitrates, chlorates and perchlorates of
ammonia, hydrazine, guanidine, etc. The selection of
the oxidizing salt depends upon the specific burning
properties desired in the propellant grain. Mixtures of
suitable inorganic oxidizing salts can be used within the
scope of this invention. The propellants may also con-
tain from 1 to about 20 percent by weight of the propel-
lant of powdered metal fuels such as powdered alumi-
num.

Various additives may be employed in preparing the
binders of this invention. For example, plasticizers,
such as, isodecyl pelargonate, polybutene, dioctyl aze-
late, bis-(2,2-dinitropropyl) formal and bis-(2,2-
dinitropropyl) acetal may be utilized. Also, catalysts
such as ferric acetylacetonate and boron trifluoride 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 propellant composition. Normally amounts of

from about 0.02 to about 0.10 percent by weight are employed. Other additives such as antioxidants, wetting agents, anti-foaming agents, etc., can be employed, if desired, in the formulation of the novel propellants.

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. 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.

Those skilled in the art will appreciate the fact that heating and cooling steps can be incorporated into the propellant processing procedure to attain optimum operating conditions for producing a given specific propellant. Likewise, various techniques which may serve to optimize the processing procedure or improve the quality of the product, e.g. vacuumizing the mixture during certain phases of the operation, can be employed if desired. The various processing steps can be carried out with standard equipment well-known to those skilled in the art. The mixer can be equipped with facilities for heating, cooling, and vacuumizing propellant batches during mixing.

There are many ways of processing the various ingredients within the scope of this invention in the formulation of propellants therefrom, and these procedures may be readily determined by those skilled in the art, depending on the precise binder, oxidizer, plasticizer, etc., selected and size of the batch to be prepared.

As noted above, from about 1 to about 15 percent by weight (total propellant weight basis), of the metallic staple are employed for purposes of this invention. The propellant binder is preferably employed in a proportion within the range from about 5 to about 55 percent and the inorganic oxidizing salt in an amount within the range from about 95 to about 45 percent by weight.

The following examples are included for purposes of illustrating the novel process and propellant composition of this invention. These examples are intended for illustration purposes only and should not be construed as limitative of the scope of the invention to the particular conditions and embodiments set forth therein.

EXAMPLE I

INGREDIENT	WEIGHT PERCENT
Ammonium perchlorate	81.50
Powdered aluminum	1.00
Isodecyl pelargonate	3.50
Lecithin	0.24
Aluminum staple (0.5×4.0×62 mil)	4.00
Copper chromite	1.50
Carboxy-terminated polybutadiene	7.40
Tris-(2-methyl aziridinyl)phosphine oxide	0.86
	100.00

To a mixer maintained at about 140°F was added the carboxy-terminated polybutadiene and the powdered aluminum. Then the ammonium perchlorate was slowly added while maintaining the temperature at about 140°F. The isodecyl pelargonate, lecithin and copper chromite were then added. The mixer was subjected to vacuum of 28 inches Hg for 20 minutes while adjusting the temperature to about 150°F. The temperature was then gradually reduced to about 125°F while maintaining the vacuum. The aluminum staple was then added

in three equal increments while maintaining the temperature at 125°F. The mixer was then scraped down, and the tris (2-methyl aziridinyl) phosphine oxide was then added. The mixer was then vacuumized for 5 minutes at 125°F and then scraped down. The vacuum was again applied for 5 minutes at 125°F. The propellant was then cast into motor casings and cured at about 150°F for three days.

EXAMPLE II

Following the procedure of Example I, the following three propellants, all of equal solids loading, were prepared. In Propellant A, no metal staple was used; in Propellant B, 3 percent staple; and in Propellant C, 5 percent staple.

Ingredient	Propellant A	Propellant B	Propellant C
Ammonium perchlorate	72.00	72.00	72.00
Powdered aluminum	15.00	12.00	10.00
Isodecyl pelargonate	3.40	3.40	3.40
Lecithin	0.20	0.20	0.20
Aluminum staple (0.5×4.0×62 mil)	—	3.00	5.00
Copper Chromite	1.50	1.50	1.50
Carboxy-terminated polybutadiene	7.20	7.20	7.20
Tris(2-methyl aziridikyl)phosphine oxide	0.70	0.70	0.70
	100.00	100.00	100.00

The burning rates of Propellants A, B and C are listed in Table I.

TABLE I

Propellant	Burning Rate (inches/sec.)
A	1.00
B	3.70
C	3.90

As can be seen from the foregoing data, the incorporation of the metal staples substantially increases the burning rate of the propellant.

In a preferred embodiment of this invention, the metallic staples prior to incorporation in the propellant are coated with a pyrotective mixture. The pyrotective coating mixture can consist of a mixture of iron and potassium permanganate or of aluminum and potassium perchlorate. The mixed powders are made to adhere to the needles by mixing the powders with a resin such as lacquer, to which a volatile thinner has been added.

One method of preparing coated needles for use in the rapid burning propellants of this invention is set forth in the following example.

EXAMPLE III

A Slurry of powdered iron (32 percent), powdered potassium permanaganate (52 percent) and lacquer (16 percent) diluted with benzene was prepared. Aluminum wire having a diameter of 8 mils is then passed through the slurry and wound on a reel at such a distance that the solvent has evaporated. The wires are then cut into needles varying in length from 250 to 375 mils.

EXAMPLE IV

INGREDIENT	WEIGHT PERCENT
NH ₄ NO ₃	65.50
(HN ₃) ₂ Cr ₂ O ₇	1.80
Polyester from 7 moles of adipic acid, 3 moles of maleic anhydride and 11 moles of diethylene glycol	8.80
Styrene	2.22
Methyl acrylate	11.00
Lecithin	0.03
Methyl ethyl ketone peroxide	0.45
t-Butyl catechol	0.20
Aluminum wire — 250 mils (prepared as in Example III)	10.00
	100.00

EXAMPLE V

INGREDIENT	WEIGHT PERCENT
NH ₄ NO ₃	69.30
(NH ₄) ₂ Cr ₂ O ₇	1.90
Polyester from 7 moles of adipic acid, 3 moles of maleic anhydride and 11 moles of diethylene glycol	9.30
Styrene	2.37
Methyl acrylate	11.60
Lecithin	0.03
Methyl ethyl ketone peroxide	0.47
t-Butyl catechol	0.23
Aluminum wire — 250 mils (prepared as in Example III)	4.80
	100.00

EXAMPLE VI

INGREDIENT	WEIGHT PERCENT
Ammonium perchlorate	81.50
Aluminum staple (0.5×4.0×62 mil)	2.00
Polypropylene glycol	9.63
Glycerol monoricinoleate	1.18
Diethyl azelate	3.62
Ferric acetylacetonate	0.04
Phenyl betanaphthylamine	0.20
Lecithin	0.21
Tolylene diisocyanate	1.62
	100.00

The aluminum staple is stirred into about one-third of the required volume of polypropylene glycol and glycerol mono-ricinoleate. The mixture is prepared in a stainless steel container. Mixing is continued for about 10 minutes. The aluminum staple slurry is added to a conventional mixture equipped with facilities for heating, cooling and vacuumizing the propellant mix. The walls of the aluminum staple slurry container are scraped thoroughly. The container is rinsed with the diethyl azelate and the rinses are added to the mixture. The remaining polypropylene glycol is added to the mixer.

With the mixer off, the ferric acetylacetonate, phenyl betanaphthylamine and lecithin are added. The mixer is convered and mixed for about 15 minutes under 26 to 28 inches of vacuum, after which it is stopped and vacuum released. The oxidizer is then added, with the mixer blades in motion. After all of the oxidizer has been added, the mixer is stopped and scraped down. The propellant mass is mixed for 15 minutes at 70°F under 26 inches vacuum. The mixer is stopped and the vacuum released. The tolylene diisocyanate is added, after which the mass is mixed for 10 minutes at 70°F and 26 inches or vacuum. The vacuum is then released and the mixture is cast.

The following are other propellant formulations from which propellant grains are prepared according to methods similar to that described in the foregoing example.

EXAMPLE VII

INGREDIENT	WEIGHT PERCENT
Ammonium perchlorate	82.00
Copper staple (0.5×4.0×125 mil)	3.00
Lecithin	0.20
Phenyl betanaphthylamine	0.20
Polytetramethylene ether glycol	8.95
Glycerol monoricinoleate	1.10
Diethyl azelate	3.00
Ferric acetylacetonate	0.04
Tolylene diisocyanate	1.51
	100.00

EXAMPLE VIII

INGREDIENT	WEIGHT PERCENT
Ammonium perchlorate	81.50
Stainless steel staple (0.5×4.0×125 mil)	2.00
Polypropylene glycol	9.63
Glycerol monoricinoleate	1.18
Diethyl azelate	3.12
Ferric acetylacetonate	0.04
Phenyl betanaphthylamine	0.20
Lecithin	0.21
Copper chromite	0.50
Hexamethylene diisocyanate	1.62
	100.00

EXAMPLE IX

INGREDIENT	WEIGHT PERCENT
Ammonium perchlorate	81.50
Brass staple (0.5×4.0×250 mil)	2.00
Polypropylene glycol	9.63
Glycerol monoricinoleate	1.18
Diethyl azelate	3.62
Ferric acetylacetonate	0.04
Phenyl betanaphthylamine	0.20
Lecithin	0.21
Tolylene diisocyanate	1.62
	100.00

EXAMPLE X

INGREDIENT	WEIGHT PERCENT
Ammonium perchlorate	81.50
Zirconium staple (0.5×4.0×62 mil)	2.00
Polypropylene glycol	9.63
Glycerol monoricinoleate	1.18
Diethyl azelate	3.12
Ferric Acetylacetonate	0.04
Phenyl betanaphthylamine	0.20
Lecithin	0.21
Copper chromite	0.50
Tolylene diisocyanate	1.62
	100.00

EXAMPLE XI

INGREDIENT	WEIGHT PERCENT
Hydrazine perchlorate	81.50
Iron staple (1.0×4.0×100 mil)	2.50
Polypropylene glycol	9.63
Glycerol monoricinoleate	1.18
Diethyl azelate	3.12
Ferric acetylacetonate	0.04
Phenyl betanaphthylamine	0.20
Lecithin	0.21
Tolylene diisocyanate	1.62
	100.00

EXAMPLE XII

INGREDIENT	WEIGHT PERCENT
Ammonium perchlorate	81.50
Hafnium staple (1.0×5.0×200 mil)	2.00
Polypropylene glycol	9.63
Glycerol monoricinoleate	1.18
Diocetyl azelate	3.12
Ferric acetylacetonate	0.04
Phenyl betanaphthylamine	0.20
Lecithin	0.21
Copper chromite	0.50
Durene diisocyanate	1.62
	100.00

The following two examples represent preferred formulations for the propellants of my invention.

EXAMPLE XIII

INGREDIENT	WEIGHT PERCENT
Ammonium Perchlorate	81.50
Powdered Aluminum	1.00
Aluminum Staple (3.0×4.0×250 mil)	4.00
Copper Chromite	1.50
Isodecyl Pelargonate	3.50
Lecithin	0.20
Carboxy terminated polybutadiene (M.W.=6000)	7.93
Succinic Anhydride-Diethanol Amine Adduct	0.07
Tris(N-1',2'-Butylene)Trimesamide	0.20
Tris(1-Aziridinyl)Phosphine Oxide	0.10
	100.00

EXAMPLE XIV

INGREDIENT	WEIGHT PERCENT
Ammonium Perchlorate	81.50
Powdered Aluminum	1.00
Aluminum Staple (0.5×4.0×62 mil)	4.00
Copper Chromite	1.50
Isodecyl Pelargonate	5.00
Succinic Anhydride-Diethanol Amine Adduct	0.12
Carboxy terminated polybutadiene (M.W.=6000)	6.49
Bis(1,2-Propylene)Isocyanate	0.19
Tris(1-Aziridinyl)Phosphine Oxide	0.20
	100.00

It will be understood that various modifications may be made in this invention without departing from the spirit thereof or the scope of the appended claims.

I claim:

1. A solid propellant composition which comprises a cured intimate mixture or a non-metallic oxidizing salt, a resin binder, and as a burning rate additive, elongated metallic staples having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, and in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

2. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin binder which is the reaction product of a carboxy-terminated polydiolefin polymer and an imine curing agent, and as a burning rate additive, elongated metallic staples having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, in an amount effective to increase the burning rate up to an amount not greater than that

equivalent to about 15 percent by weight of the propellant composition.

3. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a polyurethane resin binder, and as a burning rate additive, elongated metallic staples having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

4. A solid propellant composition which comprises a cured intimate mixture of a solid non-metallic oxidizing salt 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 capable of polymerizing with an isocyanate as determined by the Zerewitinoff method, 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 as a burning rate additive, elongated metallic staples having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about fifteen percent by weight of the propellant composition.

5. A solid propellant composition which comprises a cured intimate mixture of elongated aluminum staples, a solid non-metallic oxidizing salt, and a resin binder which comprises the reaction product of an aromatic diisocyanate, a polyether having a molecular weight between about 400 and 10,000 and a trihydroxy cross-linker compound; the aluminum staple being present in an amount effective to increase the burning rate up to an amount not greater than about 15 percent by weight, the resin binder being present in an amount between about 5 and about 55 percent by weight, and the solid non-metallic oxidizing salt being present in an amount between about 95 and about 45 percent by weight, all percentages being given on a total propellant weight basis.

6. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin binder, and as a burning rate additive, elongated metallic staples of circular cross-section having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, a diameter of from about 2.0 to about 10 mils and a length of from 50 to about 500 mils, and in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

7. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin binder which is the reaction product of a carboxy-terminated polydiolefin polymer and an imine curing agent, and as a burning rate additive, elongated metallic staples of circular cross-section, having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, a diameter of from about 2.0 to about 10 mils and a length of from 50 to about 500 mils, in an amount effective to increase the burning rate up to an

amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

8. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a polyurethane resin binder, and as a burning rate additive, elongated metallic staples of circular cross-section, having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

9. A solid propellant composition which comprises a cured intimate mixture of a solid non-metallic oxidizing salt 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 capable of polymerizing with an isocyanate as determined by the Zerewitinoff method, 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 as a burning rate additive, elongated metallic staples of circular cross-section, having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, a diameter of from about 2.0 to about 10 mils and a length of from 50 to about 500 mils, in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

10. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin binder, and as a burning rate additive, elongated metallic staples of rectangular cross-section having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, measure from 0.4 to about 5.0 mils on the short side, from about 1.0 to about 20 mils on the long side and are from about 50 to about 500 mils in length, and in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

11. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin binder which is the reaction product of a carboxy-terminated polydiolefin polymer and an imine curing agent, and as a burning rate additive, elongated metallic staples of rectangular cross-section having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, measure from 0.4 to about 5.0 mils on the short side, from about 1.0 to about 20 mils on the long side and are from about 50 to about 500 mils in length, in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

12. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a polyurethane resin binder, and as a burning rate additive, elongated metallic staples of rectangular cross-section having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C, measure from 0.4 to about 5.0 mils on the short side, from about 1.0 to

about 20 mils on the long side and are from about 50 to about 500 mils in length, in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

13. A solid propellant composition which comprises a cured intimate mixture of a solid non-metallic oxidizing salt 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 capable of polymerizing with an isocyanate as determined by the Zerewitinoff method, 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 as a burning rate additive, elongated metallic staples of rectangular cross-section having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm) and a melting point above about 600°C measure from 0.4 to about 5.0 mils on the short side, from about 1.0 to about 20 mils on the long side and are from about 50 to about 500 mils in length in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

14. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin binder, and as a burning rate additive, elongated metallic staples having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm.), a melting point above about 600°C, said elongated metallic staples being coated with a pyrotechnic mixture selected from the group consisting of a mixture of iron and potassium permanganate, and a mixture of aluminum and potassium perchlorate, said staples being present in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

15. A solid propellant composition which comprises a cured intimate mixture of a solid non-metallic oxidizing salt 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 capable of polymerizing with an isocyanate as determined by the Zerewitinoff method, 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 as a burning rate additive, elongated metallic staples having a heat conductivity of from about 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm.), a melting point above about 600°C, said elongated metallic staples being coated with a pyrotechnic mixture selected from the group consisting of a mixture of iron and potassium permanganate, and a mixture of aluminum and potassium perchlorate, said staples being present in an amount effective to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

16. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin-binder which is the reaction product of a carboxy-terminated polydiolefin polymer and an imine curing agent, and as a burning rate additive, elongated metallic staples of circular cross-section, having a heat conductivity of from about 0.10 to about 1.05 gram-

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cal/(sec)(sq.cm.)(°C/cm.), and a melting point above about 600°C, a diameter from about 2.0 to about 10 mils and a length of from about 50 to about 500 mils, said elongated metallic staples being coated with a pyrotechnic mixture selected from the group consisting of a mixture of iron and potassium permanganate, and a mixture of aluminum and potassium perchlorate, said staples being present in an effective amount to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

17. A solid propellant composition which comprises a cured intimate mixture of a non-metallic oxidizing salt, a resin binder which is the reaction product of a carboxy-terminated polydiolefin polymer and an imine curing agent, and as a burning rate additive, elongated

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metallic staples of rectangular cross-section having a heat conductivity of from 0.10 to about 1.05 gram-cal/(sec)(sq.cm.)(°C/cm.), and a melting point above about 600°C, measuring from about 0.4 to about 5.0 mils on the short side, from about 1.0 to about 20 mils on the long side and from about 50 to about 500 mils in length, said elongated metallic staples being coated with a pyrotechnic mixture selected from the group consisting of a mixture of iron and potassium permanganate, and a mixture of aluminum and potassium perchlorate, said staples being present in an effective amount to increase the burning rate up to an amount not greater than that equivalent to about 15 percent by weight of the propellant composition.

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