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[54] PROPELLANT COMPOSITIONS CONTAINING A METAL NITRITE BURNING RATE CATALYST

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[58] **Field of Search** ..... 52/.5, 8, 13, 14, 16, 18, 18 P; 149/19, 20

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EXEMPLARY CLAIM

1. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of an ammonium salt selected from the group consisting of ammonium chlorate, perchlorate and nitrate and unsaturated polyester resin consisting of the condensation product of saturated polyhydric alcohol and polycarboxylic acid heteropolymerized with an unsaturated compound selected from the group consisting of lower alkenes, lower alkynes, phenyl substituted lower alkenes, lower alkyl dienes, lower alkenyl esters of lower alkanoic acids, lower alkyl esters of lower alkenoic acids, lower alkenyl esters of lower alkenoic acids, allyl diglycol carbonate, diallyl diglycollate, and mixtures thereof; from 0 percent to about 2 percent by weight ammonium dichromate and from about 0.5 percent to about 5 percent by weight of a burning rate acceleration catalyst selected from the group consisting of potassium nitrite, barium nitrite, calcium nitrite and mixtures thereof.

7 Claims, No Drawings

PROPELLANT COMPOSITIONS CONTAINING A METAL NITRITE BURNING RATE CATALYST

This invention relates to new burning rate catalysts for solid propellant compositions.

Propellant compositions in use at the present time are composed essentially of two main components, namely a resin fuel and an oxidizing material. The fuel component is generally an organic polymer such as an alkyd resin. Due to the smokeless manner in which they burn, solid, inorganic, non-metallic oxidizers such as ammonium nitrate, ammonium perchlorate and ammonium chlorate are preferred.

The desirability of a rapid burning rate propellant for such purposes as rocket and ordnance projection has long been appreciated in propellant manufacture. Heretofore, however, only moderate burning rates have been obtained from propellants oxidized with solid, inorganic, non-metallic oxidizers. For example, ammonium nitrate oxidized propellants having burning rates in excess of 0.10 in. sec^{-1} have not been obtained even through burning rate acceleration catalysts such as ammonium dichromate are employed.

We have now found that nitrites such as potassium, calcium and barium nitrite and mixtures thereof in amounts of as little as 1 percent by weight more than double the burning rate of solid, inorganic, non-metallic salt oxidized propellants and in amounts of about 5 percent by weight increase the burning rate as much as three to fourfold. These catalysts are particularly valuable when employed in combination with conventional burning rate acceleration catalysts such as ammonium dichromate, however, their use is not limited to this individual embodiment of the invention.

These burning rate catalysts are particularly useful, although not necessarily limited in their use, in propellant compositions utilizing an alkyd resin type fuel. Such compositions are ordinarily composed of three principal ingredients, namely, an alkyd resin, an olefinic monomer and an ammonium oxidizing salt.

The alkyd resin is usually a polyester prepared by the condensation of a polycarboxylic acid with a polyhydric alcohol, one or both of which contain olefinic linkages. The unsaturation present in the ester is necessary to permit cross linking with the olefinic monomer. Among the unsaturated polycarboxylic acids which are ordinarily used in the preparation of such polyesters are maleic, fumaric, citraconic, mesaconic, itaconic acid, etc. Saturated acids found to be useful are such acids as oxalic, malonic, succinic and glutaric, etc. The polyhydric alcohols useful are dihydric alcohols such as ethylene glycol, propylene glycol, glycol, etc.; as well as trihydric alcohols such as glycerol; tetrahydric alcohols such as the erythritols; pentahydric alcohols such as arabitol, etc., or mixtures of any of these alcohols.

The olefinic component of the fuel may be, for example, styrene, vinyl acetate, acrylic acid esters, methacrylic acid esters, allyl compounds such as allyl diglycol carbonate, diallyl maleate, diallyl glycollate, and other unsaturated components such as propylene, butadiene, as well as the acetylenes. In addition derivatives of any of the above substances which are capable of polymerization with the resin may also be used. In general, any unsaturated compound compatible with the resin, and which will polymerize with it, is suitable; this includes all unsubstituted olefins and, in addition, many substituted olefins. The unsaturation present in the polyester permits it to polymerize with the double bond in the olefin, thus forming cross linkages. When a sufficient amount of cross linkage occurs the resin becomes thermosetting; and with a lesser degree of cross linkage, the resin may be thermoplastic; and, in some cases, the resin possesses properties of both thermoplastic and thermosetting resins. All of these types are within the purview of the present invention.

The oxidizers useful for this invention are the ammonium chlorate, perchlorate and nitrate salts. The oxidizer is dispersed in a finely divided condition throughout the fuel in amounts of from about 50 percent to about 80 percent by weight of the total composition. Optimum results are obtained when there is sufficient oxygen in the propellant to oxidize all of the carbon to carbon monoxide and one-third of the hydrogen to water.

The burning rate acceleration catalyst is preferably present in an amount of from about 0.5 percent to about 5 percent of the total weight of the propellant. If desired, the catalyst may be coated with combustible plastics such as nylon or methyl methacrylate. Particularly good results are obtained by mixing the potassium nitrite with finely divided carbon.

It is desirable in some instances to employ a small amount of ammonium dichromate in addition to the nitrite catalysts of our invention. When such mixtures are employed, they should ordinarily be present in an amount of from about 2.5 percent to about 7 percent by weight of the total propellant composition, the preferred amount being about 3 percent by weight.

The propellant grains are prepared by blending together the polyester and olefinic components of the fuel, the oxidizer and the burning rate catalyst. If desired, a polymerization catalyst may also be added. The mixture is cast into a mold and the fuel allowed to polymerize at a temperature in the range of from about 25° C. to about 100° C., and preferably at a temperature below 60° C.

The polymerization catalysts usually employed are organic peroxides such as benzoyl peroxide, lauryl peroxide, acetobenzoyl peroxide, ditertiary butyl peroxide, methyl ethyl ketone peroxide, 1-hydroxy-cyclohexyl hydroperoxide, cumene hydroperoxide, cycloalkane hydrocarbon peroxide, and peresters such as tertiary butyl perbenzoate and diperphthalate.

Various ingredients may also be added for specific purposes without departing from the scope of this invention. For example, lecithin may be added to improve the castability of the uncured propellant. t-Butyl catechol or cobalt octoate may also be added as polymerization modifiers.

The propellant grains prepared in the above described manner can withstand rough handling and will perform satisfactorily at temperatures in the range of from about −65° F. to about 165° F.

To illustrate the effect of the catalysts of this invention upon the burning rate of solid propellants and thereby more clearly explaining the invention, a propellant was prepared having the following formulation:

Component	Propellant I Wt. %
Ammonium Dichromate	1.99
Ammonium Nitrate	72.79
Polyester, by wt. %	9.79
47.00% Diethylene glycol	
49.45% Adipic acid	
3.55% Maleic anhydride	
Styrene	2.66
Methyl Acrylate	12.22
Polymerization Catalyst	0.49
Cobalt Octoate and Lecithin	0.06
Total:	100.00

As a matter of convenience in establishing a burning rate standard, ammonium dichromate was incorporated into the propellants used for illustration.

The burning rates effected by the addition of the catalysts of this invention are set forth in Table I. It is to be understood, however, that these examples are presented merely as a means of illustration and are not intended to limit the scope of the invention in any way.

TABLE I

Combustion Catalyst	% By Wt. of Catalyst added	Burning rate in. sec^{-1} 1000 p.s.i.
—	—	0.07
Potassium nitrite	5	0.29

Finely divided carbon	0.5	
Potassium nitrite (nylon coated)	5	0.23
Potassium nitrite	1	0.16
Potassium nitrite (methyl methacrylate coated)	1	0.16
Potassium nitrite (nylon coated)	1	0.16
Potassium nitrite (dried fuel and oxidizer)	1	0.15
Barium nitrite (magnesium sulfate coated)	1	0.12
Calcium Nitrite	1	0.13

The use of these nitrite catalysts is not limited by the particular fuel components contained in the propellants. Polymers of the polynitro alkenes and nitro-containing esters as well as other combustible polymeric materials may be used without departing from the scope of the invention. Due to the great increase in the burning rates induced by the catalysts of this invention, it is apparent that these catalysts will find widespread application in the manufacture of solid propellants.

We claim:

1. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of an ammonium salt selected from the group consisting of ammonium chlorate, perchlorate and nitrate and unsaturated polyester resin consisting of the condensation product of saturated polyhydric alcohol and polycarboxylic acid heteropolymerized with an unsaturated compound selected from the group consisting of lower alkenes, lower alkynes, phenyl substituted lower alkenes, lower alkyl dienes, lower alkenyl esters of lower alkanoic acids, lower alkyl esters of lower alkenoic acids, lower alkenyl esters of lower alkenoic acids, allyl digylcol carbonate, diallyl diglycollate, and mixtures thereof; from 0 percent to about 2 percent by weight ammonium dichromate and from about 0.5 percent to about 5 percent by weight of a burning rate acceleration catalyst selected from the group consisting of potassium nitrite, barium nitrite, calcium nitrite and mixtures thereof.

2. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of ammonium nitrate, and unsaturated polyester resin consisting of the condensation product of diethylene glycol, adipic acid and maleic anhydride heteropolymerized with a mixture of styrene and methyl acrylate and a mixture of potassium nitrite and ammonium dichromate in an amount of from about 2.5 percent to about 7 percent by weight of the total propellant composition.

3. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of ammonium nitrate, and unsaturated polyester resin consisting of the condensation product of diethylene glycol, adipic acid and maleic anhydride heteropolymerized with a mixture of styrene and methyl acrylate and a mixture of calcium nitrite and ammonium dichromate in an amount of about 3 percent by weight of the total propellant composition.

4. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of ammonium nitrate, and unsaturated polyester re sin consisting of the condensation product of diethylene glycol, adipic acid and maleic anhydride heteropolymerized with a mixture of styrene and methyl acrylate and a mixture of barium nitrite and ammonium dichromate in an amount of about 3 percent by weight of the total propellant composition.

5. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of ammonium nitrate, and unsaturated polyester resin consisting of the condensation product of diethylene glycol, adipic acid and maleic anhydride heteropolymerized with a mixture of styrene and methyl acrylate and potassium nitrite in an amount of from about 0.5 percent to about 5 percent by weight of the total propellant composition.

6. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of ammonium nitrate, and unsaturated polyester resin consisting of the condensation product of diethylene glycol, adipic acid and maleic anhydride heteropolymerized with a mixture of styrene and methyl acrylate and barium nitrite in an amount of from about 0.5 percent to about 5 percent by weight of the total propellant composition.

7. A solid propellant composition consisting essentially of a cured intimate mixture of from about 50 percent to about 80 percent by weight of the total propellant composition of ammonium nitrate, and unsaturated polyester resin consisting of the condensation product of diethylene glycol, adipic acid and maleic anhydride heteropolymerized with a mixture of styrene and methyl acrylate and calcium nitrite in an amount of from about 0.5 percent to about 5 percent by weight of the total propellant composition.

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