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PROPELLANT COMPOSITIONS

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This invention relates to solid smokeless propellants useful for rocket propulsion and has for its object to improve and increase the burning rates of such propellants.

In the operation of jet motors it is customary to burn solid propellant charges in the motor chambers to produce gas under pressure which escapes at high velocity, generally through an exhaust nozzle leading from the chamber, thereby producing thrust.

Generally propellants useful for this purpose comprise intimate mixtures of finely divided oxidizers, uniformly distributed in a resinous binder which acts as a fuel. The oxidizer is mixed with the monomer or lower molecular weight, polymerizable unit of the fuel, and then polymerized to produce a solid propellant grain.

In propellant grains commonly in use at present the oxidizer is ordinarily a metal containing inorganic oxidizing salt such as potassium perchlorate, ammonium dichromate, potassium nitrate, etc. The use of these salts produces burning rates of a sufficient magnitude to produce the required amount of thrust in combustion. However, in addition to being considerably more expensive than the non-metallic salts, these metal containing salts all possess one very undesirable property, namely, the production of large quantities of visible smoke due to the formation of metal oxides during combustion.

The use of non-metallic salts such as ammonium nitrates and ammonium perchlorate in propellant grains is well known to eliminate the production of smoke, however, these oxidizing salts exhibit extremely low burning rates and hence are unsuitable for use in propellant compositions.

We have now found a class of burning rate catalysts whose presence in non-metallic grains will increase the burning rates of such compositions by as much as 100%, thereby making practical the use of non-metallic inorganic oxidizing salts in solid propellants.

Substances useful for the acceleration catalyst of this invention are mixtures consisting of ammonium dichromate and silicon or titanium compounds capable of yielding oxides of those elements upon heating. The oxides thus formed are believed to act as cracking catalysts for the combustibles and provide increased surface area, thereby effectively increasing the overall burning rate of the propellant as much as 100% in some cases.

Although some of the compounds employed in the burning rate acceleration catalyst contain metal radicals, the elements are present in such limited quantities that they do not produce visible smoke during combustion.

The silicon and titanium compounds which are particularly useful in our propellants for improving burning rates are the lower alkyl silicones such as methyl, ethyl, propyl, isopropyl, etc., silicones and the corresponding titanates such as methyl titanate, ethyl titanate, etc. The particular organic radicals are of little importance since the active groupings useful for the catalytic purpose are the



and

radicals.

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Other siliceous compounds suitable for this purpose are lower alkyl ortho silicates such as methyl, ethyl, propyl, isopropyl, etc., silicates; as well as inorganic silicates such as calcium silicate, diatomaceous earth, silica gel, amine treated clay, and bentonite clay treated with aliphatic amines. In addition, lower alkyl and lower alkoxy siloxanes are also found to be useful.

Titanium compounds found to be useful for this purpose are the lower alkyl titanates.

Mixtures of these compounds and compositions have also been found to be useful.

The burning rate acceleration catalyst is present preferably in an amount of from about 0.5% to 5.0% by weight of the total propellant compositions. Optimum results are obtained when the catalyst is comprised of a mixture of from about 1.0 to 50.0% by weight of ammonium dichromate, the remainder being the siliceous or titanium component.

Suitable oxidizers for smokeless propellants are inorganic non-metallic salts, as for example: ammonium and hydrazine salts of nitrates, chlorates and perchlorates. For the practice of this invention, the preferred oxidizer is ammonium perchlorate.

The oxidizer should ordinarily be supplied in sufficient quantities at least to oxidize all of the carbon in the resin fuel to carbon monoxide and $\frac{1}{3}$ of the hydrogen to water. The amount of oxidizer added to the resinous mixture usually lies between 45% and 90% by weight of the total propellant composition and the weight of the fuel mixture should lie between 55% and 10% of the same propellant composition.

The fuel in which the oxidizer is dispersed is preferably a resin comprised of a polyester component, that is, the condensation product of a polybasic carboxylic acid and a polyhydric alcohol, in which there is incorporated an olefinic component.

The polyester component, sometimes known as the alkyd component, ordinarily possesses some degree of unsaturation in the molecule in order to permit polymerization with the olefinic component which may be for example; styrene, vinyl acetate, acrylic acid esters, methacrylic acid esters, allyl compounds such as allyl diglycol carbonate, diallyl maleate, diallyl glycolate, and other unsaturated components such as propylene butadiene, acetylene, etc.; as well as derivatives of any of the above substances which are capable of polymerization with the resin. In general any olefin 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 the resulting unsaturated polyester to polymerize with the double bond in the vinyl, allyl, or other olefinic additives. When a sufficient amount of cross linkage occurs the resin becomes thermosetting. 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 of resins are within the purview of the present invention.

The polyester component can be made in general as follows: The hydroxy groups of dihydric or polyhydric alcohols are permitted to condense, with the polycarboxylic groups of, for example, a dicarboxylic acid, or a mixture of dicarboxylic acids, thereby producing an unsaturated polyester. Although the polyhydric alcohol and polycarboxylic acid will react in stoichiometric proportions, it is usually a better practice to employ an excess of the alcohol.

The unsaturation permitting the polyester to polymerize with the monomeric vinyl, allyl or other olefinic component may be supplied by employing either an unsaturated polyhydric alcohol or an unsaturated dicarbox-

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ylic acid. The usual and preferred manner is to condense mixtures of an unsaturated polycarboxylic acid or anhydride and a saturated or aromatic polycarboxylic acid, or anhydride, with a polyhydric alcohol.

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

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

Aromatic dibasic acids such as phthalic anhydride, naphthalic acid, and isomers of phthalic acid can be used in the same manner as the unsaturated aliphatic acids. These materials cannot be used as the unsaturated monomer inasmuch as aromatic compounds, although unsaturated, do not undergo addition polymerization.

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

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

The condensation of the polyhydric alcohol and polycarboxylic acid is usually conducted in the presence of the monomeric vinyl, allyl or other olefinic component which form cross linkages between the polymeric chains of the polyester. The amount of olefinic monomer may range from about 25% to about 100% by weight based on the weight of the monomer-resin mixture, and the amount of the monomer to be used in each case is determined by the particular properties which are desired in the finished resin. In general, 50% by weight of polyester to 50% by weight of the olefinic additive produces a satisfactory polyester type of matrix for the propellant. The olefinic monomers listed above are all liquids and thereby serve as solvents for the heavier alkyd resin, thus facilitating the dispersion of the oxidizer throughout the liquid resin before curing.

The propellant is preferably compounded as follows: The oxidizer required to oxidize the fuel to the proper degree is uniformly mixed into the polyester resin-olefinic monomer mixture. Mixing is continued at room temperature until all of the oxidizer has been added and the mixture has a uniform consistency. A catalyst capable of accelerating polymerization of the resin mixture is added thereto and intimately incorporated therein before or at the time the oxidizer is added. In the same fashion the burning rate expediting catalyst of the present invention is added to the monomer in finely divided form. All of these substances including the oxidizer are thoroughly mixed with the liquid monomer and the resultant mixture is then cast into a suitable mold and the propellant substance cured.

The cast propellant is generally cured at temperatures ranging from ambient to about 220° F. When lower temperatures are employed the cure requires considerable time to cure. If shorter cure times are desired a

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more elevated temperature can be used. The time and temperature for curing makes no substantial difference in the ultimate product insofar as its ballistic properties are concerned.

A series of catalyzed propellants were investigated to determine the effect of the herein described catalytic mixture and its various components upon the burning rate of representative propellant mixtures. The composition by weight percent of the propellant mixtures is as follows:

Propellant Composition A:		Weight percent
Ammonium perchlorate	-----	85.00
Polyester resin	-----	3.58
Consisting of, by weight percent:		
diethylene glycol	-----	43.0
adipic acid	-----	44.25
maleic anhydride	-----	1.75
n-Butyl acrylate	-----	9.33
Methyl acrylate	-----	1.44
Methyl amyl ketone peroxide (polymerization catalyst)	-----	0.40
Lecithin	-----	0.25
		100.00

Propellant Composition A:		Weight percent
Ammonium perchlorate	-----	84.88
Polyester resin	-----	3.71
Consisting of, by weight percent:		
diethylene glycol	-----	43.0
adipic acid	-----	44.25
maleic anhydride	-----	1.75
n-Butyl acrylate	-----	9.45
Methyl acrylate	-----	1.48
Methyl amyl ketone peroxide (polymerization catalyst)	-----	0.21
Lecithin	-----	0.27
		100.00

The results of these tests are as follows:

Catalyst	Percent added	Propellant	Burning rates, 1,000 p.s.i. and 60° F. in. sec. ⁻¹
None	-----	A	0.40
Ethyl silicate	1	A	0.86
Ammonium dichromate	1	B	0.50
½ ethyl silicate and ½ ammonium dichromate	1.5	A	0.96

It may be observed from the foregoing table of burning rates that the burning rate of the propellant has been increased by the use of ammonium dichromate-siliceous catalysts more than 100%. Moreover, it is evident that the catalytic effect of the ammonium dichromate-silicate mixture is greater than could be predicted from the catalytic behaviour of its respective components. The increase in burning rate induced by 1.5% of the catalytic mixture provided by this invention is equal to the sum of the increases effected by the individual use of its two substituents in amounts of 1% respectively.

From the foregoing discussion it is evident that the burning rate acceleration catalysts of the present invention will find valuable use in any gas generating propellant type compositions such as nitro-cellulose base propellants and other nitro substituted resin-containing propellants.

It should be understood that the foregoing examples, although describing certain specific embodiments of the invention, are provided primarily for purposes of illustration and are not intended to impose any limitations upon its broader aspects.

We claim:

1. A solid propellant composition comprising a cured intimate mixture of ammonium perchlorate and a polyester resin consisting of the condensation product of di-

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ethylene glycol, adipic acid, and maleic anhydride, heteropolymerized with n-butyl acrylate and methyl acrylate; said ammonium perchlorate being present in an amount of from about 45% to about 90% and said polyester resin being present in an amount of from about 55% to about 10% and a mixture of from about 1.0% to about 50% by weight of ammonium dichromate and from about 99% to about 50% by weight of ethyl silicate in an amount of 2.0% by weight of the total propellant composition.

2. A solid propellant composition comprising a cured intimate mixture of from about 45% to about 90% by weight of the total propellant composition of a solid, non-metallic, inorganic oxidizing salt, and from about 55% to about 10% by weight of an unsaturated polyester resin consisting of the condensation product of saturated polyhydric alcohol and polycarboxylic acid heteropolymerized with lower alkyl ester of lower alkenoic acid; and from about 0.5% to about 5.0%, for example, of a burning rate acceleration catalyst consisting of a mixture of from about 1.0% to about 50% of ammonium dichromate and from about 99% to about 50% by weight of alkyl orthosilicate.

3. A solid propellant composition comprising a cured intimate mixture of from about 45% to about 90% by weight of the total propellant composition of a solid, non-metallic, inorganic oxidizing salt, and from about 55% to

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about 10% by weight of an unsaturated polyester resin consisting of the condensation product of diethylene glycol, adipic acid and maleic anhydride heteropolymerized with a mixture of n-butyl acrylate and methyl acrylate; and from about 0.5% to about 5.0% of a burning rate acceleration catalyst consisting of a mixture of from about 1% to about 50% by weight of ammonium dichromate and from about 99% to about 50% by weight of alkyl orthosilicate.

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