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PROPELLANT COMPOSITIONS

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This invention relates to solid smokeless propellants useful for rocket propulsion, and has as its object a method for reducing the dependency of the burning rate upon environmental conditions.

In the operation of jet motors it is customary to burn solid propellant charges in the motor chamber to produce gas under pressure which escapes at high velocity, ordinarily through an exhaust nozzle leading from the chamber, thereby producing a resultant thrust which propels the missile. To be useful in missiles such as rockets, shells, aircraft, etc., it is essential that the propellant used exhibit a uniform burning rate and specific impulse under vastly different environmental conditions in order that accurate control and reproduction of results may be obtained. Obviously to achieve such uniformity it is necessary that the propellant be as nearly independent of uncontrollable and unpredictable environmental conditions as is possible. The major difficulty with smokeless propellant substances heretofore in use has been their susceptibility to relatively small changes in temperature and pressure.

I have found that the incorporation of certain alkaline earth metal phosphate salts into a smokeless alkyd resin type propellant results in a propellant composition whose burning rate exhibits a high degree of independence to environmental conditions of temperature and pressure.

The inorganic salts found to be useful as ballistic modifying agents in the practice of this invention include tricalcium phosphate, calcium pyrophosphate, calcium metaphosphate, and tribarium phosphate, as well as mixtures thereof in amounts of from about 0.50% to about 2.0% by weight of the total propellant composition.

The addition of such salts to alkyd resin type propellant compositions has been found to reduce the dependency of burning rates upon temperature as much as 40° in some cases, thereby providing propellant substances which are smokeless and whose uniformity of specific impulse permits their use as propellants requiring a high degree of uniformity in ballistic properties.

The improved solid propellants of this invention make practical the use of inexpensive smokeless solid propellants in guided missiles requiring uniform speed, duration of thrust, acceleration and range, a use which has been heretofore virtually impossible except in extremely limited application.

Solid propellant compositions utilizing metal-containing oxidizing salts such as potassium perchlorate, potassium dichromate and other similar salts all possess desirable ballistic properties which would permit their use for these purposes, however, the large quantities of smoke produced during combustion preclude their use for certain purposes in military application.

Propellant compositions of this invention containing only negligible amounts of smoke-producing metals exhibit the ballistic properties necessary for such uses without the highly undesirable production of smoke, thereby enabling their use in military applications.

The propellant grains of this invention may in many instances replace the commonly used liquid fuels, thereby eliminating the necessity of complex pumping arrangements as well as the storage and handling of hazardous liquids with little or no loss in control or efficiency of performance.

In general, the solid propellant of this invention is composed of an intimate mixture of a finely divided nonmetallic solid inorganic oxidizing salt uniformly distributed in a resinous binder and the ballistic modifying agent. The oxidizers suitable for use in these improved propellants are the nitrate and perchlorate salts of ammonia.

The oxidizer should ordinarily be supplied in sufficient quantities at least to oxidize all of the carbon in the resin fule to carbon monoxide and ⅓ 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, a 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 type 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 dicarboxylic 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.

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.

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

For the polyhydric alcohol component any of the following alcohols may be used: dihydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol; 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 alcohol-acid 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 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 ballistic modifying additive 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 charge requires considerable time to cure. If shorter cure times are desired a 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.

Other components such as burning rate acceleration catalysts, polymerization modifiers, wetting agents to improve the castability of the composition, etc., may be added without departing from the scope of the invention.

For the purpose of illustrating the effect of phosphate salts of alkaline earth metals upon the ballistic properties of propellants, a series of representative compositions were prepared, having the following formulations:

Propellant A:	Percent by weight
Ammonium perchlorate	75.00
Polyester	12.35
Diethylene glycol	47.00
Adipic acid	49.45
Maleic anhydride	3.55
Styrene	12.35
Cumene hydroperoxide (polymerization catalyst)	0.25
Lecithin (wetting agent)	0.05
	100.00

Propellant B:	Percent by weight
Ammonium nitrate	72.79
Ammonium dichromate	1.99
Polyester	9.79
Diethylene glycol	47.00
Adipic acid	49.45
Maleic anhydride	3.55
Styrene	2.44
t-Butyl catechol (polymerization modifier)	0.25
Methyl acrylate	12.22
Lecithin (wetting agent)	0.03
Methyl ethyl ketone peroxide (polymerization catalyst)	0.49
	100.00

Propellant C:	Percent by weight
Ammonium perchlorate	76.00
Copper chromite (burning catalyst)	0.15
Polyester	14.11
Diethylene glycol	47.00
Adipic acid	49.45
Maleic anhydride	3.55
t-Butyl catechol (polymerization modifier)	0.40
Styrene	8.59
Cumene hydroperoxide (polymerization catalyst)	0.25
Dioctyl sodium sulfosuccinate (wetting agent)	0.50
	100.00

These propellants were burned with and without an alkaline earth phosphate salt being incorporated in them. The results of the burning tests are shown in Table I.

TABLE I

Propellant	Catalyst	Percent added	u	π_p	n	p.s.i.a.
A	None		0.12	0.22	0.44	500
A	do		0.15	0.27	0.44	1,000
A	$Ca_3(PO_4)_2$	1	0.09	0.12	0.22	500
A	$Ca_3(PO_4)_2$	1	0.11	0.14	0.22	1,000
A	$Ca_3(PO_4)_2$	1	0.07	0.09	0.21	500
A	$Ca_3(PO_4)_2$	1	0.10	0.13	0.21	1,000
A	$Ca_3(PO_4)_2$	0.5	0.12	0.19	0.39	500
A	$Ca_3(PO_4)_2$	0.5	0.13	0.13	0.0	1,000
A	$Ca_3(PO_4)_2$	2	0.07	0.10	0.31	500
A	$Ca_3(PO_4)_2$	2	0.10	0.15	0.31	1,000
A	None			0.27	0.45	500
A	$Ba_3(PO_4)_2$	1		0.17	0.38	500
B	None		0.21	0.41	0.50	1,000
B	$Ca_3(PO_4)_2$	0.5	0.08	0.16	0.38	1,000
C	None		0.21	0.40		800
C	$Ca_3(PO_4)_2$	1	0.14	0.30		800
C	None		0.30	0.42		800
C	$Ca_3(PO_4)_2$	1	0.16	0.21		800
C	$Ca_2P_2O_7$	1	0.19	0.25		800

u and π_p are temperature coefficients relating the burning rate and the temperature of the propellant. A reduction in the numerical values of these coefficients indicates a decrease in the dependency of the burning rate toward said temperature.

u, the temperature coefficient at constant chamber pressure, is usually calculated from burning conducted under controlled experimental conditions such as a Crawford bomb in which constant pressure is maintained by the regulation of the inert atmosphere. It relates the burning rate to propellant temperature as follows:

$$u=\frac{\text{Percent change in burning rate at constant pressure}}{1^\circ\text{ F. change in propellant temperature}}$$

n, the burning rate exponent, relates the dependency of the burning rate upon environmental pressure as follows:

$$n\cong\frac{\log(r_2/r_1)}{\log(p_2/p_1)}$$

wherein r_1 is the burning rate at pressure p_1 (p.s.i.a.), and r_2 is the burning rate at pressure p_2.

π_p, the temperature coefficient of burning at constant area ratio, is usually calculated from burning conducted in a motor permitting varying pressure and defined by:

$$\pi_p=\frac{\text{Percent change in chamber pressure}}{1^\circ\text{ F. change in propellant temperature}}$$

and related to u by the approximation:

$$\pi_D = \frac{u}{1-n}$$

It can be seen from a comparison of the coefficients calculated from the burning of the treated and untreated propellants set forth above, that the addition of a phosphate salt of alkaline earth metals substantially decreases the dependency of the burning rate upon both temperature and pressure.

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.

I claim:

1. An improved solid propellant composition consisting of a cured intimate mixture of from about 45% to about 90% by weight of the total propellant composition; a non-metallic solid inorganic oxidizing salt; from about 55% to about 10% by weight of a polyester resin consisting of the condensation product of diethylene glycol, adipic acid, and maleic anhydride; heteropolymerized with styrene; and from about 0.5 to about 2.0% by weight of tricalcium phosphate.

2. An improved solid propellant composition consisting of a cured intimate mixture of from about 45% to about 90% by weight of the total propellant composition; a non-metallic solid inorganic oxidizing salt; from about 55% to about 10% by weight of a polyester resin consisting of the condensation product of diethylene glycol, adipic acid, and maleic anhydride; heteropolymerized with styrene and methyl acrylate; and from about 0.5 to about 2.0% by weight of tricalcium phosphate.

3. An improved solid propellant composition consisting of a cured intimate mixture of from about 45% to about 90% by weight of the total propellant composition; a non-metallic solid inorganic oxidizing salt; from about 55% to about 10% by weight of a polyester resin consisting of the condensation product of diethylene glycol, adipic acid, and maleic anhydride; heteropolymerized with styrene; and from about 0.5% to about 2.0% by weight of calcium pyrophosphate.

4. An improved solid propellant composition consisting of a cured intimate mixture of from about 45% to about 90% by weight of the total propellant composition; a non-metallic solid inorganic oxidizing salt; from about 55% to about 10% by weight of a polyester resin consisting of the condensation product of diethylene glycol, adipic acid, and maleic anhydride; heteropolymerized with styrene; and from about 0.5% to about 2.0% by weight of tribarium phosphate.

5. A solid propellant composition comprising 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 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 alkenoic acids, lower alkenyl esters of lower alkanoic acids, lower alkyl esters of lower alkenoic acids, allyl diglycol carbonate, diallyl diglycolate and mixtures thereof; and a ballistic modifying agent selected from the group consisting of tricalcium phosphate, calcium pyrophosphate, tribarium phosphate, and mixtures thereof in an amount of from about 0.5% to about 2.0% by weight of the total propellant composition.

6. A solid propellant composition which comprises from about 45% to about 90% by weight of the total propellant composition of a solid, non-metallic, inorganic oxidizing salt selected from the group consisting of, ammonium perchlorate, ammonium nitrate and mixtures thereof, 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 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 alkenoic acids, lower alkenyl esters of lower alkanoic acids, lower alkyl esters of lower alkenoic acids, allyl diglycol carbonate, diallyl diglycolate and mixtures thereof; and a ballistic modifying agent selected from the group consisting of tricalcium phosphate, calcium pyrophosphate, tribarium phosphate and mixtures thereof in an amount of from about 0.5% to about 2.0% by weight of the total propellant composition.

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