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BURNING RATE CATALYSTS FOR SOLID PROPELLANT COMPOSITIONS

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This invention relates to a new burning rate acceleration catalyst for solid propellant compositions.

Solid, non-metallic propellant compositions are used for rocket and ordnance projection, as well as for assisted aircraft take-offs. Such propellant compositions are composed essentially of two main components; namely, a combustible organic resin fuel and an oxidizing material. In use, such propellants are enclosed within a chamber and ignited whereby large quantities of gases are formed. These gases are exhausted through an orifice thereby giving propulsive force to the vehicle in the opposite direction.

The fuel component of the propellant needs only to be combustible and possess physical properties which permit it to be cast or molded into a propellant grain. A wide variety of resins, such as asphalt, polyesters, polyalcohols, polynitroalkenes, and mixtures thereof, are useful for this purpose.

The oxidizing material is usually an inorganic oxidizing salt. Metal salts, such as potassium perchlorate, are often used; however, upon combustion they form solid particles which create large quantities of visible smoke. Smoke is highly undesirable for military purposes of concealment. Hence, non-smoking, non-metallic, inorganic oxidizing salts such as hydrazine and ammonium salts are preferred in such applications.

The desirability of rapid burning propellants for rocket and ordnance projections is well established. Metal-containing oxidizers generally provide fast burning compositions. Unfortunately, propellants utilizing the non-metallic, inorganic oxidizing salts as the oxidizer have heretofore exhibited only relatively slow burning rates. For example, ammonium nitrate oxidized propellants have never been known to burn at rates in excess of 0.10 in./sec., even though combusted in the presence of burning rate acceleration catalysts such as ammonium dichromate.

We have now found that the burning rates of the highly desirable non-metallic propellants can be increased as much as 100% by incorporating small amounts of a perchlorate salt of iron, cobalt, chromium, manganese, silver, copper or mixtures thereof in the formulation. These burning rate acceleration catalysts are used in the compositions in such small amounts, usually from about 0.5% to about 5% by weight of the composition, that the smoke formed by their combustion is negligible. The catalysts of this invention 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 particular embodiment of the invention.

Oxidizers useful in the practice of this invention are non-metallic chlorate, perchlorate, and nitrate salts such as ammonium nitrate, ammonium chlorate, ammonium perchlorate and hydrazine nitrate. The non-metallic nitrate salts are preferred due to their availability, stability

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and the ease with which they can be handled. The nitrate salts, however, usually do not burn as rapidly as the chlorate or perchlorate salts.

The oxidizer, in a finely divided condition, is dispersed throughout the fuel component of the propellant. Ordinarily, the oxidizer is present in an amount of from about 45% to about 90% by weight of the total composition. Optimum results are obtained when there is sufficient oxygen in the propellant to oxidize all of the carbon in the fuel to carbon monoxide and one-third of the hydrogen to water.

Combustible organic resinous fuels useful in propellant compositions of this invention include: asphalt, polymers and copolymers of alkenes, arylalkenes, alkynes, alkenyl diglycols, alkyl alkenoates, alkenyl alkenoates, alkenoamides, and amidoalkenyls, and unsaturated alkyd resins heteropolymerized with the above compounds.

Asphalts having softening points of about 180° F. to about 220° F., and penetration values of about 7 to 9 mm./5 sec./100 gm. at a temperature of 720° F., are usually preferred for rocket fuel due to their ballistic properties. When castability and low expansion coefficients are not essential, other grades of asphalt can be used. To improve the physical properties of the asphalt, a condensation product of sebacic acid and a polyhydric alcohol, a wax such as cetyl acetamide, or a hydrocarbon oil is often incorporated into the asphalt. Suitable fuels of this type are more fully disclosed in assignee's copending application Serial No. 634,609, filed December 12, 1945, and assignee's United States Patent No. 2,565,269, issued August 7, 1951.

A typical formulation by weight percent of an asphalt base propellant composition is as follows:

Propellant composition A

	Percent
Ammonium perchlorate	75.0
Asphalt	10.5
Cetyl acetamide	3.0
Castor oil	8.0
Diethyl sebacate	3.5
	100.0

The asphalt-base propellant grains are prepared by heating the asphalt until soft, ordinarily about 350° F., stirring in the oxidizers and additives, and then permitting the mixture to harden in a mold.

Polyalkenoamides and amidoalkenyls useful as fuels include: N,N-dimethyl acrylamide, N-methyl acrylamide, N-nitro-N-methyl acrylamide, acrylamide, N,N-diallyl formamide and N,N-dimethyl vinyl carbamate. Suitable fuels of this type are more fully disclosed in assignee's copending application Serial No. 392,472, filed November 16, 1953.

A typical formulation of a propellant composition having a polyamide fuel component is as follows:

Propellant composition B

	Percent
Ammonium nitrate	76.81
N,N-dimethyl acrylamide	22.94
Methyl amyl ketone peroxide (polymerization catalyst)	0.25
	100.00

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The polyamide propellant grain is prepared by mixing the amide, oxidizer and polymerization catalyst until a homogeneous mixture is obtained and curing the mixture at a temperature of from about 25° C. to about 100° C.

Polyalkenes useful as fuels include: polyisobutylene, butadiene-styrene copolymers, butadiene-acrylonitrile copolymers, and isobutylene-isoprene copolymers. Suitable fuels of this type are more fully disclosed in assignee's copending application Serial No. 637,004, filed December 22, 1945, now abandoned.

A typical formulation of a propellant composition having a polyolefinic fuel component is as follows:

Propellant composition C

Ammonium perchlorate	Percent
Copolymer	76.00
	24.00
	Percent
Isobutylene	98.5
Isoprene	1.5
	100.0
	100.00

The polyolefin-base propellant grain can be prepared by roll milling the oxidizer into the polyolefin until a homogeneous mixture is obtained and then pressing the material into sheets or discs.

Polyalkenoates useful as fuels include: polymers and copolymers of acrylic acid, acrylic acid esters, methacrylic acid and methacrylic acid esters. Suitable fuels of this type are more fully disclosed in assignee's copending application Serial No. 321,943, filed November 21, 1952, now abandoned.

A typical formulation of a propellant composition having a polyester fuel component is as follows:

Propellant composition D

Hydrazine nitrate	Percent
Methyl acrylate	60.00
Allyl diglycol carbonate	25.60
Methyl methacrylate	3.60
t-Butyl peroxide (polymerization catalyst)	10.40
	0.40
	100.00

The polyester-base propellant grain is prepared by mixing the various monomers, oxidizer and polymerization catalyst until a homogeneous mixture is obtained, and subsequently curing the mixture in a mold.

Alkyd resin fuels are polyesters prepared by the condensation of polycarboxylic acid and polyhydric alcohol, one or both of which contain some unsaturation. Among the unsaturated polycarboxylic acids which are ordinarily used in the preparation of such polyesters are maleic, fumaric, citraconic, mesaconic, itaconic acids, etc. Saturated acids found to be useful include such acids as oxalic, malonic, succinic, glutaric, etc. Mixtures of saturated and unsaturated acids are usually preferred. 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; penta-hydric alcohols such as pentaerythritol, etc.; or mixtures of any of these alcohols.

The olefinic component of the fuel can be, for example, styrene, vinyl acetate, acrylic acid esters, methacrylic acid esters, allyl compounds such as allyl diglycol carbonate, allyl maleate, diallyl diglycolate, and other olefinic components such as propylene and butadiene, as well as acetylenes. 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. Suitable fuels of this type are more fully disclosed in assignee's copending application Serial No. 109,409, filed August 9, 1949.

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A typical formulation of a propellant composition utilizing an alkyd resin fuel is as follows:

Propellant composition E

5	Ammonium dichromate	Percent
	Ammonium nitrate	1.99
	Polyester, by wt. percent	72.79
		9.79
		Percent
10	Diethylene glycol	47.00
	Adipic acid	49.45
	Maleic anhydride	3.55
		100.00
15	Styrene	2.66
	Methyl acrylate	12.22
	Methyl amyl ketone peroxide	0.49
	Cobalt octoate and lecithin	0.06
20	Another typical formulation is:	100.00

Propellant composition F

	Ammonium dichromate	2.00
25	Ammonium nitrate	76.00
	Polyester resin, by wt. percent	5.82
		Percent
	Diethylene glycol	47.00
	Adipic acid	49.45
30	Maleic anhydride	3.55
		100.00
	Styrene	2.79
	Methyl acrylate	12.49
35	Methyl ethyl ketone peroxide	0.40
	Lecithin	0.40
	Cobalt octoate	0.10
		100.00

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

It is preferred to employ a polymerization catalyst to hasten the reaction. The polymerization catalysts usually employed in such propellant compositions are organic peroxides such as benzoyl peroxide, lauryl peroxide, acetobenzoyl peroxide, ditertiary butyl peroxide, methyl ethyl ketone peroxide, 1-hydroxy-cyclohexyl hydroperoxide, cumene hydroperoxide, and cycloalkane hydrocarbon peroxide, and peresters such as tertiary butyl perbenzoate and diphenylphthalate.

Various other ingredients can be added for specific purposes without departing from the scope of the invention. For example, lecithin can be added to improve the castability of the uncured propellant. t-Butyl catechol or cobalt 2-ethyl hexanoate is often added as a polymerization modifier.

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.

The particular fuel employed in the propellant composition does not affect the function of the burning rate acceleration catalyst of this invention. In addition to the propellant compositions described above, this catalyst can be used in compositions utilizing fuel components such as polymers of nitroalkenes, nitroalkynes, nitro-containing acids and their esters, as well as other combustible organic polymeric materials.

The burning rate acceleration catalysts of this invention

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are preferably incorporated into the propellant compositions in finely divided form and are mixed with the fuel usually at the same time the oxidizer is mixed. To illustrate the improvement in the burning rate brought about by incorporating these catalysts into a solid propellant, the results of a series of burning tests are shown in the table below. These tests were made using propellant E described above. In the absence of a catalyst, propellant E does not readily sustain combustion, therefore, as a matter of convenience in establishing a burning rate standard for comparative purposes, ammonium dichromate was incorporated in all of the sample grains. It is to be understood 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

Catalyst	Percent catalyst added	Burning rate in sec.-1 1,000 p.s.i.
Chromium perchlorate.....	1	0.07
Cobalt perchlorate.....	1	0.12
Ferrous perchlorate.....	1	0.13
Manganese perchlorate.....	1	0.15
Silver perchlorate.....	1	0.13
Copper perchlorate.....	1	0.12
	1	0.11

As can be seen from the data presented in the table above, a substantial increase in the burning rate of the propellant was effected by the catalysts of this invention. Increases in burning rate of the magnitude herein obtained are particularly valuable in rocketry and ordnance projection, for such projectiles are ordinarily guided only during the period of their launching. When the full thrust created by the propellant is available during this time, the projectile can be more effectively directed.

Due to the great increase in the burning rates of non-metallic, smokeless propellant compositions induced by the above catalysts, and their applicability to propellants having a wide variety of fuel components, it is apparent that these catalysts will find extended and valuable use in the field of rocketry and ordnance propulsion.

We claim:

1. A solid, smokeless propellant composition comprising a cured, intimate mixture of from about 45% to about 90% by weight solid, non-metallic, inorganic oxidizing salt, from about 10% to about 35% by weight combustible, organic resin selected from the group consisting of:

- (a) asphalt;
- (b) olefinic polymers;

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- (c) alkyl alkenoate heteropolymerized with olefin;
- (d) unsaturated polyester resin consisting of the condensation product of saturated polyhydric alcohol and polycarboxylic acid heteropolymerized with an unsaturated compound; and
- (e) alkenoamide polymers;

and from about 0.5% to about 5.0% by weight of a burning rate acceleration catalyst selected from the group consisting of the perchlorate salts of iron, cobalt, chromium, manganese, silver, copper and mixtures thereof.

2. The composition of claim 1 wherein the burning rate acceleration catalyst is chromium perchlorate.

3. The composition of claim 1 wherein the burning rate acceleration catalyst is cobalt perchlorate.

4. The composition of claim 1 wherein the burning rate acceleration catalyst is iron perchlorate.

5. The composition of claim 1 wherein the burning rate acceleration catalyst is manganese perchlorate.

6. The composition of claim 1 wherein the burning rate acceleration catalyst is silver perchlorate.

7. The composition of claim 1 wherein the burning rate acceleration catalyst is copper perchlorate.

8. The composition of claim 1 wherein the combustible organic resin is asphalt.

9. The composition of claim 1 wherein the combustible organic resin is an olefinic polymer.

10. The composition of claim 1 wherein the combustible organic resin is alkyl alkenoate heteropolymerized with an olefin.

11. The composition of claim 1 wherein the combustible organic resin is an unsaturated polyester resin consisting of the condensation product of saturated polyhydric alcohol and polycarboxylic acid heteropolymerized with an unsaturated compound.

12. The composition of claim 1 wherein the combustible organic resin is an alkenoamide polymer.

13. The composition of claim 1 wherein the non-metallic, inorganic oxidizing salt is selected from the group consisting of nitrate, perchlorate and chlorate salts of ammonia and hydrazine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,479,828 Geckler ----- Aug. 23, 1949

OTHER REFERENCES

Audrieth: "The Chemistry of Hydrazine," John Wiley & Sons, New York (1951), p. 189.
Friederich et al.: Z. ges. Schiess-Sprengstoffwesen, vol. 21 (1926), pp. 49-52; 85-87.