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ROCKET PROPELLANT

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The present invention relates to propellants for rockets, guided missiles, assisted takeoffs for aeroplanes, and the like. It particularly relates to a resinous composition formed by polymerizing polymers or copolymers of free radical polymerizable compounds with suitable organic oxidizing agents incorporated therein so as to give a powerful and effective propellant for rockets and jet-driven missiles.

The castings or grains used in rockets and jets are necessarily large, frequently weighing several hundred pounds and sometimes weighing several tons. The problem of making such a casting is subject to numerous complications. In the first place, the casting generally has to be one solid piece so as to burn evenly and regularly. It cannot have flaws, such as air pockets, cracks, or unevenly dispersed compounds because they would produce an uneven rate of burning and would seriously interfere with navigation of the rocket or plane.

These castings also, by their very nature, are quite explosive and must be very delicately handled. At no stage of their manufacture can they be heated much above certain critical limits. The larger the casting the greater is the difficulty for removal of heat and the greater the tendency for cracks or flaws and the greater is the tendency for explosion to occur. Prior to the present invention, when large blocks of resins were polymerized in the mold, the heat evolved during polymerization was excessive. A large propelant casting was liable to explode. Only under excruciating circumstances, therefore, could propellants be manufactured from these resins. Accordingly, the propelants were manufactured by utilizing oxidizing agents dispersed or combined with nitro cellulose or similar non-polymerizing compounds which were nonfluid non-castible materials. As is readily evident, such a step is expensive or time-consuming or solvent removal is difficult when utilized for making large castings or grains. In accordance with the present invention, I have found a mixture of oxidizing agent or agents with a combustible polyester-olefine resin having relatively low unsaturation which provides combustible propellant grains or pieces of remarkable uniformity.

Another requirement of propellants is that they burn to complete combustion and have no smoke. This is usually a military necessity to hide movement of jet planes and rockets and to facilitate take-off from restricted areas.

It is another object of this invention to provide a smokeless propellant for military use.

It is another object of the present invention to provide an inexpensive and easily manufactured propellant.

Other objects will be apparent from the following description of the invention.

In accordance with the present invention, I have found that copolymers of (1) a polyester binder and (2) a free radical polymerizable mono-olefinic compound (3) mixed with a sufficient oxidizing agent to burn or oxidize at least one-fourth of the hydrogen atoms therein to water and all of the carbon atoms to carbon monoxide provides an exceptional propellant. Suitable polyester binders are a condensation product of a polyhydric alcohol such as ethylene glycol and preferably diethylene glycol, with a mixture of saturated and unsaturated aliphatic dibasic acids having the saturated and unsaturated acids in particular molar proportions as hereinafter set forth. Suitable mono-olefinic compounds that are polymerizable by free radicals include styrene, methyl acrylate, methyl methacrylate, and other acrylic and methacrylic esters, and acrylo and methyl acrylo nitriles, and especially the nitroalcohol esters of acrylic acid such as the ester of acrylic acid and beta nitro ethanol and its higher homologs.

The oxidizing agents present are preferably largely of organic type so as to provide smokeless burning although inorganic oxidizing agents may be used alone or in admixture with the organic type. A saturated nitro aliphatic or aromatic compound such as nitroparaffin, PETN, etc. supplemented with a saturated nitro aliphatic alcohol ester of acrylic or methacrylic acid in the polymer is especially desirable. Nitro aliphatic materials of especial importance are 2,2-dinitropropane and 2,2-dinitropropanediol.

The unsaturated polyester component that is copolymerized with the olefinic compound, contains an average of only one polymerizable olefinic group, i.e., one double bond conjugated to oxygen for each 40 to 275 atoms in the polyester chain. In this connection, benzene group and organic rings, although these are preferably absent in the polyester component, are considered to have a chain length of four atoms.

The shrinkage and exotherm in the polyester binder is greatly increased as the proportion of olefinic groups in the polyester chain is increased. When the number of olefinic groups is less than 1 for each 275 atoms, the amount of cross-linking between the polymerizable olefinic compound (mono or diolefinic) is not great enough to give the desired rapidity of gel formation and the desired compatibility between the constituents of the product. When the number of olefinic groups is more than 1 per 125 to 130 chain atoms, superior compatibility results. When the number of olefinic groups is more than 1 for each 40 atoms in the polyester chain, the tendency for explosions probably from the exothermic heat of polymerization given off becomes too great. Preferably, there should be not more than one bond for each 50 carbon atoms to obtain the best results of gelation and noncracking. Cracks or separations from the mold occur in larger castings when the number of olefinic groups is greater than 1 for each 40 atoms in the polyester chain. In my preferred resins, therefore, I have one such double bond for about 50 to about 125 or 130 chain atoms.

The polyester may be prepared by esterifying a mixture of any saturated aliphatic dicarboxylic acid, having carboxyl groups connected by an aliphatic hydrocarbon group of at least 4 carbon atoms in length (although adipic acid is somewhat superior) and a relatively small proportion of an alpha beta unsaturated dicarboxylic acid such as maleic acid preferably as anhydride with any dihydric alcohol, such as ethylene glycol or preferably diethylene glycol. The molar quantity of polyhydric alcohol should preferably be just slightly in excess of the total mols of acid present, an excess of between .02 and .1 mol for each total mol of acid is preferred. Esterification may be accomplished by simply heating the mixture and stirring in a vessel with a reflux condenser adapted to permit the escape of water vapor. The viscosity increases as the heating is continued. The rise in temperature indicates the extent of the reaction. The polyester thus prepared is mixed with a substantial amount of liquid olefinic compound free radical forming catalyst and oxidizing agent and allowed to polymerize to form a propellant of the present invention.

The amount of polymerizable olefinic compound mixed with polyester also determines the hardness of the resinous material. Harder resinous materials are produced with increased amounts of olefinic material when the olefine is itself hard-setting.

The saturated dicarboxylic acids used in forming the polyester propellant of this invention should at least largely consist of aliphatic acids as aromatic acids are not desirable, at least in major proportion, as they give a product which is too rigid for propellant use. The saturated aliphatic dicarboxylic acids may have from 4 to 12 carbon atoms between carboxylic groups. Examples of saturated aliphatic dicarboxylic acids include adipic acid and decanedioic acid (sebacic acid). Adipic acid is preferred.

The preferred oxidizing agents are PETN (pentaerythritol tetra nitrate), RDX (cyclotrimethylene trinitroamine), Tetryl (2,4,6, trinitrophenyl methyl nitroamine), dinitro propane and other organic oxidizing agents. Suitable inorganic oxidizing agents include persalts, such as potassium perchlorate, ammonium perchlorate, ammonium persulfate, and other recognized oxidizing agents, such as ammonium nitrate. The oxidizing agents should not dissolve in the binder and should always be evenly dispersed therethrough.

The oxidizing agents for smokeless operation should be incorporated into the binder so that at least one-fourth and preferably one-half of the hydrogen atoms are oxidized or burned to water, and all of the carbon atoms are oxidized to carbon monoxide. An oxidizing agent that is insoluble in the polymerizable materials is preferred. If necessary, the catalyst and dispersing agents, such as the long chain amines, or the like, may be present to facilitate the casting operation.

Any of the monomer soluble peroxide or hydroperoxide catalysts may be used including benzoyl peroxide, cumene hydroperoxide, methyl-ethyl ketone peroxide, acyl peroxide, aldehyde peroxides, and alkyl peroxides. A metal activator such as an amine and iron or a cobalt or manganese salt of an organic acid such as cobalt linoleate, cobalt naphthenate or other cobalt, iron, or manganese salt soluble in monomer may be present to accelerate the reaction if desired.

The catalyst should ordinarily be present in relatively small amounts, such as .01 to .2%. The speed of the polymerization reaction is also generally a function of catalyst content and initial temperature. The casting operations, of necessity, must be extended over a sufficient period of time to dissipate the heat of polymerization, and for this reason proper thermal dynamic balance is necessary. This latter factor usually controls the amount of catalyst and desirability for activator. In order to prepare uniform propellants the viscosity of the polyester-mono olefinic mix should be sufficient to permit good casting and yet not permit settling of the solid oxidizing agents present. I have found that the viscosity of the mixture at the time of casting i.e., when oxidizing agents are admixed therewith should be between 40 and 300 cps. at 77° F. to provide a homogenous casting.

The following examples illustrate the present invention:

Example 1

	Mols
Diethylene glycol	1.06
Adipic acid	.79
Maleic anhydride	.21

The maleic anhydride, adipic acid, and diethylene glycol were incorporated in a reaction vessel equipped with a reflux condenser maintained at sufficiently elevated temperature to permit the escape of water vapor without causing condensation thereof. The ingredients were heated slowly under an atomsphere of inert gas, such as nitrogen, carbon dioxide, etc., to a rapid evolution of water vapor, and the heat supplied was maintained sufficient to cause this vigorous evolution without much increase in temperature. The initial temperature leveled off at about 120° C. and the vessel was maintained at this temperature for several hours. As the reaction progressed, the temperature continued to rise until after 20 hours it reached 250° C. The ingredients in the vessel were maintained at this temperature until a viscosity of a mixture of the polyester with an equal amount of styrene was 65±15 cps. at 77° C.

One-third of the polyester thus prepared was mixed with the following ingredients:

RDX (cyclotrimethylene trinitroamine)	4 mols.
Styrene	1.9 mols.
Ammonium nitrate	4 mols.
Benzoyl peroxide	About .1% of the weight of the styrene.

This mixture was poured into a mold and maintained at room temperature for several hours until polymerization was complete.

Another third of the polyester thus prepared was mixed with the following compounds:

Ethyl acrylate	1.4 mols.
PETN (pentaerythritol tetra nitrate)	2 mols.
Ammonium nitrate	3 mols.
Cumene hydroperoxide	.1% of the weight of the polymerizable constituents.

Another third of the polyester prepared above was mixed with the following compounds:

Methyl acrylate	1.6 mols.
RDX	12 mols.
Potassium perchlorate	3 mols.
Cumene hydroperoxide	1% of the weight of the acrylate.

All three propellant mixes thus prepared are allowed to stand in a room at 40° C. until even-burning, solid grains are produced. The proportions of each mixture were 60% polyester and 40% monomer. In the above examples other olefinic compounds and oxidizing agents, such as Tetryl, PETN, RDX, potassium chlorate and ammonium nitrate can be substituted in whole or in part for the oxidizing equivalents.

Example 2

The following polyester was prepared as in Example 1:

	Gram mols
Diethylene glycol	.97 to 1.2
Adipic acid	.78 to .8
Maleic anhydride	.18 to 2.1

The proportions are selected so that the molar amount of the ploy glycol is then charged in molar excess in an amount of .01 to .08 mol over the total mols of the acid present. The ester was prepared as in Example 1 to a viscosity of 40 to 300 cps. at 77° F. when mixed with an equal amount of styrene monomer and to an acid number of 4 to 20. The product (ester) has a refractive indext of 1.4790±.001. This ester was divided into three parts, and to the first part was added the following compounds:

	Mols
Styrene	11.7
RDX	66.6
Ammonium nitrate	12

To a second part was added:

Methyl acrylate	9.8
RDX	23.3
Ammonium nitrate	3.5

and to the last part was added:

Beta nitro ethyl acrylate	8.4
RDX	20
Ammonium nitrate	10

In the above propellant compounds the polyester comprised about 20% of the total by weight and the monomer about 80%. As before, the oxidizing agents and olefinic compounds can be substituted by their molar equivalents.

Example 3

The following polyester was prepared as in Example 2 except for the ingredients being changed.

	Mols
2 methyl 2,4 pentanediol	1.1
Sebacic acid	1.0
Maleic anhydride	.2

To the above polyester was added the following co-monomer and oxidizing agents:

Styrene	1.9 mols.
PETN (pentaerythritol tetra nitrate)	4 mols.
Ammonium nitrate	4 mols.
Cumene hydroperoxide	1% based on said styrene.
Dispersing agent (21 carbon aliphatic amine)	1% based on said styrene.

The solids were dispersed in the monomeric mixture. This mixture was cast into molds and allowed to polymerize to a solid state by standing in a room maintained at 50° C.

Example 4

To the total mols of polyester of Example 2, the following mixture was added:

	Gram mols
Methyl acrylate	8.8
2,2 dinitro propane	1.9
PETN	5.6

together with 10 grams of 60% methyl ethyl ketone peroxide as a catalyst, and the mixture polymerized to a hard colorless mass at 60° C.

Example 5

The following mixture was prepared:

	Mols
Beta nitro methyl acrylate	3.7
2,2 dinitro propanediol 1,3	.46
Tetryl (2,4,6 trinitrophenyl methyl nitroamine)	30
Ammonium nitrate	5

To the above was added: 5 grams of benzoyl peroxide as a catalyst and the mixture allowed to polymerize to a colorless mass at 60° C.

Example 6

A polyester was made as set forth in Example 2. 100 parts by weight of this polyester was mixed with an equal amount by weight of styrene and parts by weight of finely divided potassium perchlorate and 1 percent based upon the polymerizable materials of benzoyl peroxide. The mixture thus prepared was cast in cylindrical molds and allowed to remain at an elevated temperature of about 40° until the mixture is hardened to a tough or rubbery state. The propellant thus made was placed in the combustion chamber of a jet capable of directing the exhaust gases in a single direction through a nozzle and ignited. The thrust on the jet motor showed the propellant to exhibit extremely desirable characteristics.

In the claims the term "maleic acid" is intended to include maleic anhydride.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and therefore it is not intended to be limited except as in the following claims.

I claim:

1. A propellant consisting essentially of (1) a copolymer of 40 to 60 parts of a polyester and 60 to 40 parts of a mono-olefinic compound selected from the group consisting of styrene, methyl acrylate, methyl methacrylate, beta nitro ethyl acrylate, acrylonitrile, and methyl acrylonitrile, said polyester being the condensation product of a mixture comprising diethylene glycol, a saturated aliphatic carboxylic acid of at least 6 carbon atoms and having carboxyl groups connected by a hydrocarbon chain, and an alpha-beta-unsaturated dicarboxylic acid in which mixture the molar quantity of said glycol is approximately equal to the total molar quantity of said acids and in which mixture the unsaturated acid is proportioned to the saturated acid so that in the polyester chain there will be but one olefinic group for each 40 to 130 atoms in the polyester chain, said polyester being further characterized in that when mixed with an equal quantity of monomeric styrene the mixture thus formed has a viscosity of 40 to 300 cps. at 77° F. and an acid number of 4 to 20, and (2) an oxidizing agent consisting essentially of a mixture of at least one organic explosive selected from the group consisting of pentaerythritol tetra nitrate, cyclotrimethylene trinitro amine, (2,4,6) trinitrophenyl methyl nitroamine and dinitro propane and at least one solid inorganic oxidizing salt which gives off oxygen on heating, the total oxidizing agent present being sufficient to combine with one-half of the hydrogen atoms to form water and to combine with all of the carbon atoms to form carbon monoxide, said solid oxidizing salt being intimately disperse through said copolymer.

2. A propellant for rockets and jets consisting essentially of (1) a copolymer of from 40 to 60 parts of a polyester and 60 to 40 parts of styrene, said polyester being the condensation product of a mixture comprising diethylene glycol, adipic acid and maleic acid, the ingredients of said mixture being proportioned to provide .97 to 1.2 moles of diethylene glycol and .78 to .8 mole of adipic acid for each .18 to .21 mole of said maleic acid, said esterification product being further characterized in that when mixed with an equal quantity of monomeric styrene the mixture thus formed has a viscosity of 65 plus or minus 15 cps. at 77° F., an acid number of 4 to 20 and a refractive index of 1.4790±.001 and (2) an oxidizing agent consisting essentially of a mixture of at least one organic explosive selected from the group consisting of pentaerythritol tetra nitrate, cyclotrimethylene trinitro amine, (2,4,6) trinitrophenyl methyl nitroamine and dinitro propane and at least one solid inorganic oxidizing salt which gives off oxygen on heating, the total oxidizing agent present being sufficient to combine with one-half of the hydrogen atoms to form water and with all of the carbon atoms to form carbon monoxide, said oxidizing agent being intimately dispersed through said copolymer.

3. A propellant for rockets and jets consisting essentially of (1) a copolymer of from 40 to 60 parts of a polyester and 60 to 40 parts of styrene, said polyester being the condensation product of a mixture comprising diethylene glycol, adipic acid and maleic acid, the ingredients of said mixture being proportioned to provide .97 to 1.2 moles of diethylene glycol and .78 to .80 mole of adipic acid for each .18 to .21 mole of said maleic acid, said esterification product being further characterized in that when mixed with an equal quantity of monomeric styrene the mixture thus formed has a viscosity of about 65 cps. at 77° F. and by having an acid number of 4 to 20 and a refractive index of 1.4790±.001, (2) a solid inorganic salt capable of supplying oxygen when heated, the total oxidizing salt present being sufficient to provide the oxygen required to combine with at least one half of the hydrogen present to form water and to combine with all the carbon atoms to form carbon monoxide and being intimately dispersed through said copolymer, and (3) an organic explosive

selected from the group consisting of pentaerythritol tetra nitrate, cyclotrimethylene trinitroamine, (2,4,6) trinitrophenyl methyl nitroamine and dinitro propane.

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