

[54] **COMPOSITE PROPELLANTS CONTAINING POLYMERS OF TRINITRATOPENTAERYTHRITYL ACRYLATE**

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[57] **ABSTRACT**

Polymerizable combustible compositions, suitable for the manufacture of propellants, consisting essentially of a mixture of (1) 14 to 31 parts of trinitratopentaerythrityl acrylate, (2) 1 to 3 parts of a polymerizable monoacrylic alkyl ester having an alkyl group of four to twelve carbon atoms, (3) 10 to 26 parts of a plasticizer for poly(trinitratopentaerythrityl acrylate), said plasticizer consisting essentially of a major proportion of compounds containing nitro groups, (4) 0.1 to 2.5 parts of a soluble multiply olefinically unsaturated polyester, (5) 30 to 65 parts of a solid powdered oxidizer and (6) 0 to 25 parts of a finely particled, readily combustible solid selected from the group consisting of carbon, aluminum, magnesium, zinc, zirconium and boron.

9 Claims, No Drawings

**COMPOSITE PROPELLANTS CONTAINING
POLYMERS OF****TRINITRATOPENTAERYTHRITYL ACRYLATE**

This invention deals with compositions which provide propellants and serve as explosives, and compositions which serve as propellants, and with rocket motors which utilize propellant compositions of this invention as their source of energy.

Propellant compositions have been proposed based on gun cotton and nitroglycerin. While these may have rapid burning rates and moderately favorable specific impulses, they must be cartridge-loaded, requiring heavy accessory components which place an unnecessary load upon the rocket motor.

Also several compositions have been developed which comprise a rubbery or resinous binder and an oxidizing agent, which mixtures can be extruded into or packed into a motor casing. While these compositions are quite satisfactory for a variety of applications, such as propellants in gun shells, artillery rockets, and air-to-air rockets, they are not completely satisfactory for ground-to-air rockets and ballistic missiles which require propellants having maximum specific impulse.

The specific impulse of high performance rockets is of vital importance. For example, an increase of about 10% in specific impulse may well double the range of a ballistic missile.

In addition, the compositions of the art based on resinous binders and an oxidizing agent have been of primary interest in situations in which slow to moderate rates of burning are desirable. The burning rates of these compositions are limited so that they are not adaptable to a great variety of applications.

Yet it would be highly desirable not only to provide compositions which are characterized by high burning rates but also by ready adjustment of burning rates by simple means.

It is also necessary that a practical propellant meet other criteria, such as thermal stability, storage stability, stability during preparation, insensitiveness to impact, freedom from toxicity to workers preparing the compositions and to those using them, and low pressure and temperature coefficients of burning rates. Also, when the compositions have once been placed within a motor case, they must maintain their given form under wide extremes of temperature and they must be able to withstand the tremendous accelerations to which they will be exposed during firing.

A necessary requirement is that a propellant be formed without voids, cracks, or fissures. One consequence of such defects is that the propellant charge may detonate upon firing. Again, if a propellant possesses such faults and should be fired apparently successfully, the charge tends to break up with ejection of unburned chunks and the full energy of the propellant cannot be utilized.

To meet the above and other requirements there is first formulated a primary composition which can be stored, transported, and finally placed and cured in a motor when and where desired. The primary composition is converted into a fixed composition in the form of grains or of a grain when it is cured. This fixed composition is used as a propellant.

The primary composition is fluid as first prepared or when it is heated. In a fluid state it may be mixed with a free radical polymerization initiator, cast into a mold or a casing which serves as both mold and container,

and cured by heating. If desired, the primary composition when cast in a motor casing is case-bonded thereto and this is one of the important advantages of the compositions of this invention. During the curing step unsaturated components of the primary mixture are polymerized together. The fixed composition is stable, useful, and effective over a wide range of temperatures, such as -30° to 60°C .

The primary composition is formed by mixing together 14 to 31 parts of trinitratopentaerythrityl acrylate (petrin acrylate), 1 to 3 parts of polymerizable monoacrylic ester having as the alcohol residue an alkyl group of four to twelve carbon atoms, 10 to 26 parts of liquid plasticizer for polymerized trinitratopentaerythrityl acrylate, 0.1 to 2.5 parts of a soluble multiply olefinically unsaturated polymer, and 30 to 65 parts of an oxidizer, and if desired, 0.01 to 2 parts of stabilizer and of polymerization inhibitor. There is preferably used in addition to the above essential components from one to 25 parts of readily combustible, finely particled solid or solids. Solids are particularly useful in combustible mixtures for rocket motors, but may be omitted in explosive mixtures.

In the preparation of the primary compositions the various ingredients are weighed out as required for the particular composition to be prepared. In a preferred way of mixing the liquid plasticizer is supplied to a mixing vessel. To this are added in any convenient order the soluble multiply olefinically unsaturated polymer, the monoacrylic ester, petrin acrylate, stabilizer, and inhibitor. The resulting mixture is stirred and heated, desirably with water heated to about 75° - 80°C circulated through the mixer jacket. When the mixture becomes homogeneous, solid ingredient or ingredients are supplied. Before and/or during this step the temperature of the mixture may desirably be allowed to fall. A temperature as low as 60° - 65°C can be used while the solid material is uniformly incorporated, which comprises an oxidizer or a mixture of oxidizers. If a readily combustible solid is to be used, it is also incorporated at this point.

At this stage of the preparation there are several courses which may be followed. If the primary composition is to be stored or transported for loading in motors at other locations, the mixture may be cooled and solidified in the form of small pieces and/or packed in containers. If the primary composition is to be charged at this time to motors, it is passed in fluid form into casings and there cured.

To accelerate curing there is added to the mixture in a fluid state a polymerization initiator. This may be mixed with the fluid batch by stirring. Desirably initiator is dissolved in a portion of liquid plasticizer prior to addition to the mixture. If desired, the initiator or solution of initiator may be mixed with the primary composition while it is flowing for loading into a casing.

It is very desirable to subject the fluid mixture to reduced pressure before it is loaded. This removes gases absorbed or trapped in the fluid mixture, thereby preventing voids in the final casting. Pressures below 100 mm are desirable.

After the mixture has been degassed, it may be flowed into the casing in which it is to be used. The casing should be clean and free from grease and may be lined, if desired, with a resinous coating. Before the primary composition is run in, the casing may desirably be flushed with an inert gas such as nitrogen and is heated

to a temperature sufficient to maintain the mixture admitted thereto in a fluid state. A mandrel may be placed in the center of the casing to impart a required shape. Such mandrel is best coated to provide ready release of the mandrel after the composition has been cured. The coating is desirably one such as polytetrafluoroethylene.

The casing and contents are then cooled. The mandrel is withdrawn. The top of the propellant grain is trimmed, if necessary. An inert coating of a plastic may be applied to the trimmed top surface. The motor casing is now ready for assembly with other components of a rocket or missile or it may be stored until such time as it is to be so used. Assembly will include supplying such parts as igniter, squib, nozzle, war head, etc.

Petrin acrylate of requisite purity has become available from several types of reactions. For example, it may be prepared by reaction below 30°C of acrylyl chloride and pentaerythritol trinitrate in the presence of dimethylaniline and a solvent such as acetonitrile, methylene chloride, acetone, methyl ethyl ketone, or dioxane, or mixtures of such solvents.

In another method, pentaerythritol trinitrate and acrylic acid are reacted in the presence of a benzene-sulfonyl chloride and a trialkylamine containing a total of six to fifteen carbon atoms and having alkyl groups of not over five carbon atoms each, such as triethylamine. The reaction is carried out in the presence of a volatile organic solvent or of a water-miscible organic solvent, such as acetonitrile, acetone, methyl ethyl ketone, dioxane, methylene chloride, chloroform, or ethylene dichloride in a proportion sufficient to maintain the mixture in a fluid state. The temperatures of mixing and reacting are kept between -20° and 90°C, preferably 0° and 50°C. The ester may be precipitated by mixing the reaction mixture with water.

This ester should be free of high percentages of dinitratopentaerythryl diacrylate, but the presence of not over about two or three percent of this cross-linking agent is permissible. Thus, only a commercial grade of the ester is needed here and almost completely pure ester is not essential although it is convenient to use for purposes of control and of uniform results.

Poly (petrin acrylate) when formed as a homopolymer is hard and brittle, and by itself does not provide suitable propellant compositions even when mixed with an oxidizer.

Not all of the petrin acrylate need be in the monomeric state, rather only sufficient to ensure that the primary composition is fluid enough to flow into molds. Thus, some of the petrin acrylate may be in the form of solvent-soluble polymer. This requires that the polymeric petrin acrylate be practically free of cross-linking components.

A way to prepare freely soluble, polymeric petrin acrylate is described in a previously filed application from the same research laboratory, now Ser. No. 757,174, filed Aug. 19, 1958. According to this method a solution of trinitratopentaerythryl acrylate is prepared in a polar organic solvent such as methyl ethyl ketone, methyl propyl ketone, or tetrachloroethane. The solution is emulsified in water with the aid of an emulsifying agent. Typical non-ionic emulsifiers are water-soluble condensates of ethylene oxide with long-chained alcohols, long-chained mercaptans, alkylphenols or long-chained fatty acids or a mixture of acids such as obtained from tall oils. Typical anionic emulsifiers include

water-soluble salts of alkylbenzene-sulfonates, alkylphenoxyethyl or alkylphenyl-polyoxyethyl sulfates or sulfonates, dialkyl sulfosuccinates, or alkyl sulfates or sulfonates.

Emulsion polymerization is effected under the influence of a free radical initiator, preferably in a redox system, such as potassium, sodium, or ammonium persulfate or an organic peroxide having at least some water-solubility.

A reducing agent such as an alkali metal sulfite, metabisulfite, thiosulfate, or hydrosulfite, may be added. Also, there may be used a regulator such as octyl, dodecyl, or tetradecyl mercaptan, or an activator, such as a salt of a metal which undergoes change of valence, typical of which is iron conveniently in the form of ferrous chloride or sulfate.

The polymerization is carried out at 20° to 100°C. Polymer may be precipitated, washed with a lower alcohol, and dried.

The function of the adder polymer is to limit shrinkage of the fixed composition of cured mixture and thus avoid cracking, separation, and the like therein. Up to about two-thirds of the petrin acrylate may be supplied in this soluble form. But, in other cases none of the polymer may be used.

It has been found desirable to use a comonomer a small proportion of an acrylic ester of sufficient molecular size to impart a softening effect in the final cured composition. There may be used an ester such as *n*-butyl, *sec*-amyl, 2-ethylbutyl, hexyl, *n*-octyl, 2-ethylhexyl, 3,5,5-trimethylhexyl, decyl, or dodecyl acrylate or methacrylate. Likewise, there may be used a mixture of such a polymerizable vinylidene ester and an acrylic amide, including acrylamide itself, *N*- β -aminoethylacrylamide, *N*- β -dimethylaminoethylacrylamide, or *N*- β -ureidoethylmethacrylamide. Also, there may be used an acrylic ester having nitrogen-containing substituents to increase polarity, as in dimethylaminoethyl methacrylate, an amido-substituted ester, such as methacryloyloxyacetamidoethylethyleneurea. The polar nature of such substituents when introduced into the copolymer of the fixed compositions improves adhesion of the compositions to the casings in which they are cast.

The liquid plasticizer is preferably of the type which will help support combustion through the presence of nitro or nitrate groups. Yet not all of the plasticizer need be of this type. The plasticizing liquid must be compatible with the polymer which results when the primary composition is cured. This requires the presence of distinctly polar substituents. Typical of the plasticizing liquids which help support combustion are butanetriol trinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, tetraethylene glycol dinitrate, mixed propylene-ethylene polyglycol dinitrates, and mixtures of two or more of such liquids.

A minor proportion, usually less than a third of the liquid plasticizer, may be one or more plasticizing esters which does not contain a nitro group, yet one which will be compatible with the final copolymer. Such an ester should have sufficient polarity to be miscible with the combustion-supporting plasticizer and the polymer from trinitratopentaerythryl acrylate. Such liquids as ethyl, propyl, or butyl phthalates, azelates, or sebacates, or comparable ether esters with groups such as ethoxyethyl, propoxyethyl, butoxyethyl, or butoxyethoxyethyl may be used.

The multiply olefinically unsaturated polymers are organic solvent soluble polymers, which are primarily polyesters or polyesters dissolved in a polymerizable polyvinylidene compound. Addition polymers from maleic or fumaric acid and one or more alkylene glycols with or without another dibasic acid are well known. Useful glycols include ethylene, propylene, butylene, diethylene, and triethylene glycols or mixed glycols having ethylene and other alkylene groups. While the polyester may be a maleic-glycol condensate, it may also be a condensate of maleic acid (or anhydride), glycol, and such a dibasic acid as adipic, azelaic, sebacic, succinic, or phthalic acid.

The polyester may be supplemented with one or more polyvinylidene compounds, such as diallyl phthalate, diallyl maleate, allyl diglycol carbonate, allyl succinyl allyl glycolate, diallyl succinate, divinylbenzene, and similar polyvinylidene compounds in which the polyester is dissolved and which can itself enter into copolymerization. Mixtures in proportions from 80:20 to 25:75 by weight of polyester to polyvinylidene monomer are especially useful.

The purpose of the multiply olefinically unsaturated component is to provide the proper degree of cross-linking of the final copolymer to render it form-stable and stable against changes in temperatures, pressures, and mechanical forces encountered in handling, firing, and dispatching rocket motors. At the same time this component plays a part in bonding the final copolymer to a casing.

The oxidizer is an essential component for providing good burning and high impulse. It may be a nitrate, usually inorganic, such as ammonium, sodium or potassium nitrate, or a perchlorate such as ammonium, sodium, and potassium perchlorate or mixtures of two or more of such oxidizing agents. These may be supplemented or replaced with an organic oxidizer such as nitroguanidine, pentaerythritol tetranitrate, or cyclotri-methylenetrinitramine.

The nitrates and perchlorates are available or are readily prepared in different particle sizes. Relatively coarse particles may be used when it is desired to provide relatively slow burning rates. Some differences in burning rates also result from the choice of salt used as oxidizer.

Thus it becomes possible to provide propellant compositions which vary over the widest range of burning rates. Such control of burning rates and wide range of burning rates is possible because of the high burning rate and specific impulse which are possible as a result of the combination of ingredients or components used in the compositions of this invention.

For example, a burning rate (as determined by the Crawford-Huggett Strand Burner) of 1.2 inch per second at 1,000 psig is obtained by using as the oxidizer ammonium perchlorate having a mean particle diameter of 35 microns. On the other hand use of ammonium nitrate with an average particle size of about 300 microns gives a burning rate of 0.05 inch per second at 1,000 psig. Proportional rates are obtained with intermediate particle sizes and choice of oxidizer. These differences in burning rate have been confirmed in rocket motors. Thus, by choice of an oxidizer or mixture thereof and selection of particle size or sizes there can be prepared compositions covering a wider range of burning rates than has heretofore been possible. In this

way the compositions can be adapted to any intended use.

Oxidizer is prepared in the particle size or sizes which may be desired. If desired, the oxidizer may be dried at any stage. In general, drying at the temperature of low pressure steam (100° - 110°C) is sufficient, a moisture content of not over 0.05% being sought. If necessary, the oxidizer is crushed or ground and desirably sieved to ensure uniformity and reproducibility.

The particles of oxidizer or oxidizers may vary in size from about 5 microns to about 400 microns. In general, particles of oxidizer will pass at least a 40 mesh screen and preferably a 60 mesh screen. The particles may be fairly uniform as to size or mixtures of different sizes may be used.

The presence of stabilizer and of polymerization inhibitor in the composition is desirable, this latter particularly when the primary mixture is to be stored or shipped to a point at which it will be heated, shaped, and converted to a fixed polymeric form. The usual stabilizers for nitro compounds can be advantageously used in amount from 0.1 to about one part of the compositions. Typical stabilizers are sym-diphenyl-urea and sym-diphenyldiethylurea.

The inhibitor is one such p-methoxyphenol, hydroquinone, quinone, N-nitrosodiphenylamine, or di-β-naphthol. The proportion of inhibitor used may be determined with reference to the particular composition, the inhibitor being best proportioned to the amount of monomer present and to the length of storage of the primary mixture. Amounts from about 0.002 part to 0.1 part provide a useful range.

At such time as the primary composition is to be converted to the fixed composition, there is advantageously incorporated into the primary composition from 0.05 to 1 part of an initiator of the free radical type. As initiator there may be used an organic peroxide, such as benzoyl peroxide, acetyl peroxide, tert-butyl perbenzoate caproyl peroxide, di-tert-butyl diphenylphthalate, methyl ethyl ketone peroxide, or di-tert-butyl peroxide.

The initiator is most conveniently taken up in a small amount of a liquid plasticizer and added to the primary composition in this diluted state.

Addition of solid combustible particles to the primary composition is often highly desirable. Such particles perform a number of functions in both the primary compositions and the fixed compositions. Solid combustible particles are especially desirable and useful in large grains or individual castings. One purpose they serve is to prevent resonant burning. This avoids the need for using special equipment such as resonance rods to deal with this problem and thus avoids the added weight of such equipment. Another function of the solid particles is to supply a source of energy, since at the flame temperatures produced in the burning of these particular compositions, these particles can also burn.

The presence of the combustible solid particles provides a ballistic modifier which changes or controls ballistic characteristics which include type of burning and burning rate, specific impulse, and pressure and temperature coefficients of burning rate. Opaque solids have a definite influence on the effects of radiation.

Furthermore, the solid particles, particularly when in leaf form, may assist in suspending coarse pieces of oxidizer, as when it is desired to use an oxidizer in rela-

tively coarse form to provide a slower rate of burning. The solid particles have other influences on the physical nature of the compositions, acting as strengthening and reinforcing solids.

Useful combustible solids include carbon black, aluminum, magnesium, zinc, zirconium, and boron. When a carbon black is used, it must be selected with regard to possible inhibiting effect which it may exert against polymerization. There are some carbon blacks which so act, and others which exhibit no evident inhibiting action, as can be revealed by a simple test for polymerization by heating a polymerizable vinylidene compound with initiator and a carbon black under study.

The metals may be in the form of amorphous or crystalline powders or in leaf form, such as is used for preparing leafing pigments or powders for paints. Particle sizes may vary from about one micron with average particle sizes of about 10 to 20 microns. Leafing powders have been found effective from one completely passing a 325 mesh screen to one giving 90% through a 325 mesh screen and 95.5% through a 100 mesh screen.

Atomized or powdered metals meeting similar specifications for particle size are also useful. This form of metal has little influence on the viscosity of the primary composition when in a melted or fluid form and, therefore, permits a considerable proportion of combustible solid in the compositions without interfering with the flow of primary compositions.

On the other hand, when it is desirable to increase the viscosity of the primary composition, as, for example, when it is sought to prevent settling of other solid particles, such as particles of oxidizer, then use of flakes or leafing powders is indicated, at least to the extent still permitting flow of the heated primary composition. In many cases a mixture of a leafing powder and an atomized powder is called for because this permits use of a relatively high proportion of combustible solid particles with attendant advantages in energy relationships.

In the loading of motors, it is necessary to prepare the motor casing so that it can retain the grain formed therein during burning. A casing of metal may be cleaned with a solvent or with a detergent solution or both, and dried. In some instances it may be helpful to sand blast the metal to improve bonding to the metal. In some situations it is helpful to coat the inside surfaces of the casing with resin and insolubilize the coating by baking. One object is to provide good adhesion of the grain cast in the casing to the walls thereof. Asbestos fibers may be included in the coating to additionally insulate the motor case from heat produced during burning of the propellant.

The preparation of the several types of compositions and the preparation of motors are illustrated with the following examples which are presented for purposes of illustration and not by way of limitation. Parts are by weight unless otherwise indicated.

EXAMPLE 1a

There are charged to a jacketed kettle 17 parts of triethylene glycol dinitrate. The kettle is heated with water in the jacket at 80°C. The charge is stirred and thereto are added 1 to 6 parts of 2-ethylhexyl acrylate, 0 to 5 parts of a polyester resin composition prepared from 50% of a condensate of phthalic and maleic anhydrides and propylene glycol, and 50% of diallyl phthal-

ate, 15 parts of trinitratopentaerythryl acrylate of 98% purity, and 0.02 part of p-methoxyphenol. The temperature of the mixture is carried to 77°C whereupon the jacket is supplied with water at 65°C and the temperature of the mixture is allowed to fall to 67°C. Thereupon, there is stirred into this mixture 47.8 parts of ammonium perchlorate consisting of about an equal weight mixture of particles of 35 and of 65 microns. Thereafter, there are added 18 parts of a mixture of equal weights of aluminum leaf, 99% of which passes a 325 mesh screen, and of atomized aluminum powder, 100% of which passes a 100 mesh screen and 90% of which passes a 325 mesh screen, and 0.25 part of symdi-phenyldiethylurea. The mixture is now subjected to reduced pressure down to 20 mm.

The resulting composition can be stored as prepared or it may be passed while in a fluid state to a motor casing. The composition as prepared in combustible and can be used as an explosive.

EXAMPLE 1b

As the above mixture flows from the mixing vessel, there is mixed therewith a solution of tert-butyl perbenzoate extended with triethylene glycol dinitrate. This addition is regulated so that to a batch of the above size there is added a total of 0.09 part of the peroxidic initiator. The resulting mixture flows into a motor casing which has been sand blasted, cleaned with acetone, dried, flushed with nitrogen, and heated to about 75°C. Within the casing a mandrel has been placed to impart a desired shape at the center of the final fixed composition. When the batch has been placed within the casing, it is kept for 48 hours at 75°-80°C by an external water bath. The mandrel is withdrawn, the top of the casting is trimmed and coated with a plastic, such as polysulfide rubber, and a nozzle is attached to the casing and necessary accessories are installed.

The cured composition is a tough rubbery solid which is tightly held by the casing. When it is ignited with the aid of an igniter, it burns progressively, giving a specific impulse of 255 lbf-sec/lbm. Measurement during the firing of 49 rounds based on the above formulation gave specific impulse values up to 260 lbf-sec/lbm with a mean of 255 lbf-sec/lbm.

The fixed composition meets requirements as to stability, being chemically stable on storage and form-stable during burning. It remains rubbery over a wide temperature range (from about -40°C to 60°C). It has low shock sensitivity and low brisance.

The procedure used in Example 1 is followed for the preparation of compositions shown in Table I.

Table I

Typical Compositions Containing Ammonium Perchlorate

Ingredient	Parts by Weight				
	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Triethylene glycol dinitrate	15.9	18.0	26.0	15.9	15.9
Octyl acrylate	1.5	1.7	2.5	1.5	1.5
Petrolin acrylate	13.4	15.2	22.0	13.4	13.4
Polyester	1.2	1.3	1.9	1.2	1.2
NH ₄ ClO ₄	62.8	38.4	27.0	62.8	62.8
Aluminum	5.0	25.0	20.0	-	-
Stabilizer	0.2	0.2	0.2	0.2	0.2
Carbon black	-	-	-	5.0	-
Boron	-	-	-	-	5.0

Triethylene glycol dinitrate may be replaced with one or more other nitrated plasticizers or supplemented with one or more of the ester or ether ester plasticizers mentioned above.

The aluminum used is finely divided. In Example 2 it is in flake or leaf form, 99% of which passes a 325 mesh screen. A similar particle size is used in Examples 3 and 4, but the aluminum in these compositions is in both leaf and atomized forms. The aluminum may be replaced at least in part with finely particled zinc, zirconium, boron, or magnesium.

The ammonium perchlorate may be of any of the sizes shown as suitable. In place of ammonium perchlorate, there may be used sodium or potassium perchlorate or mixtures of two or more such oxidizers.

The polyester in these compositions is a 50% solution of a maleic acid-propylene glycol condensate in diallyl phthalate.

If desired, to any of these compositions there may be added 0.01 to 0.5 part of polymerization inhibitor. Such addition is particularly desirable when the above compositions are to be stored or transported.

To convert the above primary compositions to fixed compositions they are treated in a fluid state with tert-butyl perbenzoate and cured at 75°-80°C to give tough, rubbery solids which, when ignited, burn with a high specific impulse.

EXAMPLES 7 - 9

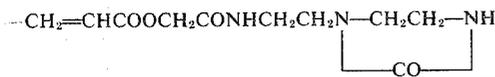
The above procedure is followed with the combinations summarized in Table II.

Table II

Typical Compositions Containing Ammonium Nitrate

Ingredient	Parts		
	Ex. 5	Ex. 6	Ex. 7
Triethylene glycol dinitrate	20	15	15
Alkyl acrylate	—	1	1
Amidoester	2	1	1
Petrin acrylate	15.3	34	33
Polyester	0.95	0.5	1
NH ₄ NO ₃	57	50	49
Aluminum	4.75	—	—
Stabilizer	—	0.5	1

As alkyl acrylate here, there is used as isononyl acrylate. The amidoester has the structure



Polyester is a soluble adipic acid-maleic-propylene glycol condensate. The aluminum is a leafing pigment, 99% of which passes a 325 mesh screen. The ammonium nitrate is crushed to pass a 100 mesh screen.

When these compositions are treated with 0.1 part of a peroxidic initiator, such as benzoyl peroxide, they are converted at 75°-80°C to tough solids which burn smoothly with good specific impulses. In place of the ammonium salt there may be used sodium or potassium nitrate or mixtures of nitrates and one or more perchlorates.

EXAMPLE 8

A composition of good burning rate and good specific impulse is prepared in accordance with the procedural steps above from 25 parts of triethylene glycol dinitrate, 2.3 parts of 2-ethylhexyl acrylate, 1.5 parts of an adipic-maleic-propylene glycol condensate, 21 parts

of petrin acrylate, 18 parts of ammonium perchlorate, 30 parts of nitroguanidine, 2 parts of aluminum leafing powder, and 0.2 parts of sym-diphenyldiethylurea.

This composition may be mixed with 0.5 part of tert-butyl perbenzoate and run into a motor casing, where it is heated at 80°C for 40 hours to give a tough rubbery casting which burns with good specific impulse.

A variation in the above type of composition is prepared from 25 parts of triethylene glycol dinitrate, 2.35 parts of 2-ethylhexyl acrylate, 1.85 parts of an adipic-maleic-propylene glycol condensate, 20.8 parts of a petrin acrylate mixture of 17 parts of monomer and 3.8 parts of solvent-soluble polymer, 38.8 parts of nitroguanidine, 11.2 parts of aluminum leaf, and 0.2 parts of stabilizer.

We claim:

1. Polymerizable combustible compositions, suitable for the manufacture of propellants, consisting essentially of a mixture of (1) 14 to 31 parts of trinitratopentaerythryl acrylate, (2) 1 to 3 parts of a polymerizable monoacrylic alkyl ester having an alkyl group of four to 12 carbon atoms, (3) 10 to 26 parts of a plasticizer for poly(trinitratopentaerythryl acrylate), said plasticizer consisting essentially of a major proportion of compounds containing nitro groups, (4) 0.1 to 2.5 parts of a soluble multiply olefinically unsaturated polyester, (5) 30 to 65 parts of a solid powdered oxidizer and (6) 0 to 25 parts of a finely particled, readily combustible solid selected from the group consisting of carbon, aluminum, magnesium, zinc, zirconium and boron.

2. Polymerizable combustible compositions, suitable for the manufacture of propellants, consisting essentially of a mixture of (1) 14 to 31 parts of trinitratopentaerythryl acrylate, (2) 1 to 3 parts of a polymerizable monoacrylic alkyl ester having an alkyl group of four to twelve carbon atoms, (3) 10 to 26 parts of a liquid plasticizer for poly(trinitratopentaerythryl acrylate), said plasticizer consisting essentially of a major proportion of compounds containing nitro groups, (4) 0.1 to 2.5 parts of a soluble multiply olefinically unsaturated polyester, (5) 30 to 65 parts of a powdered oxidizer selected from the group consisting of the ammonium, sodium, and potassium salts of nitric and perchloric acids and mixtures thereof, (6) 0 to 25 parts of a finely particled, readily combustible solid selected from the group consisting of carbon, aluminum, magnesium, zinc, zirconium and boron.

3. Polymerizable combustible compositions as set forth in claim 2 in which the plasticizer is triethylene glycol dinitrate.

4. Compositions as set forth in claim 2 which contain 0.01 to 2 parts of a chemical stabilizer for nitro compounds.

5. Compositions as set forth in claim 2 which contain 0.01 to 2 parts of a compound which inhibits the polymerization of ethylenically unsaturated compounds.

6. Propellant compositions consisting essentially of, as binder, a copolymer of (a) 14 to 31 parts of trinitratopentaerythryl acrylate, (b) 1 to 3 parts of a monoacrylic alkyl ester having an alkyl group of four to twelve carbon atoms, (c) 0.1 to 2.5 parts of a soluble multiply olefinically unsaturated polyester, said copolymer being plasticized with, 10 to 26 parts of a liquid plasticizer for poly(trinitratopentaerythryl acrylate), said plasticizer consisting essentially of a major proportion of compounds containing nitro groups, having dis-

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persed uniformly therethrough 30 to 65 parts of a powdered oxidizer selected from the group consisting of the ammonium, sodium and potassium salts of nitric and perchloric acids and mixtures thereof, and also having dispersed therethrough 0 to 25 parts of a finely particled, readily combustible solid selected from the group consisting of carbon, aluminum, magnesium, zinc, zirconium and boron.

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7. Propellant compositions as set forth in claim 6 in which there is present 1 to 25 parts of aluminum.

8. Compositions as set forth in claim 7 in which the aluminum is a mixture of a leafing powder and an atomized powder.

9. Propellant compositions as set forth in claim 6 in which the plasticizer is triethylene glycol dinitrate.

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