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3,265,543 COMPOSITE PROPELLANT CONTAINING NITROGLYCERIN

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6 Claims. (Cl. 149—19)

This invention relates to composite propellant compositions. More particularly this invention relates to new plasticized polymeric binder compositions, to composite propellants made with such binders, and to processes for preparing these compositions.

Solid propellant compositions for propelling rockets and the like are becoming increasingly important because of certain inherent advantages possessed by these propellants as contrasted with liquid propellants. Prominent among solid propellants are compositions designated collectively as composite propellants which are mixtures of fuel and oxidizer in separate phases, the oxidizer or the oxidizer and part of the fuel being finely divided solid inorganic material, and the remaining part or all of the fuel being an organic material of plastic, resinous or elastic nature. The organic fuel acts also as a binder to hold the finely divided solid components in a well mixed and uniform state of distribution and to confer tensile and compressive strengths and a sufficient degree of elasticity that the finished solid propellant compositions will withstand handling, transportation, storage, and firing without significant deformation or fragmentation. The term binder as used herein includes the plastic, resinous, and elastic matrix materials of composite propellants which hold the composition together and which have fuel value in the propellant composition.

In the manufacture of such solid propellants, the resin-like fuel-binders or their components are mixed in the fluid state with the oxidizer and other ingredients, thus making possible the shaping of the propellant composition by extrusion, rolling, casting or other processes, even though the propellant composition is composed predominantly of particulate solid material. After being thoroughly mixed and shaped, as by being extruded or being placed in a mold, the mixture is cured during a period of storage, often at an elevated temperature. The shaped plastic mass sets up to a solid during the process.

The fluid state of the binder may be achieved by incorporating it into the mixture at an elevated temperature, subsequent solidification being achieved upon cooling the composition. Or the binder may be formed by incorporating liquid intermediates which subsequently react to form the polymer in situ during the aging or storage period. Alternatively, a low molecular weight fluid prepolymer is incorporated during mixing, and this is further polymerized to form the solid binder during the aging or curing period after mixing.

Solvents for a resin-like binder may be employed to increase fluidity and facilitate mixing, the solvent being removed during the curing period, though generally with less satisfactory results because of the difficulty of removing the solvent from massive shapes of the propellant composition.

Another technique used for incorporating a binder into a composite propellant composition depends upon the use of a plastisol, that is, a liquid dispersion of finely divided resin in a plasticizer. When the mixed composition subsequently is stored or heated, the plasticizer solvates the resin particles and the mass gels into a more or less rigid structure, the physical properties of which are dependent upon the kind and amount of plastisol ingredients incorporated in the propellant composition.

Several materials have been proposed and used as

binders in the manufacture of composite propellants. Generally these are organic polymers chosen from among several types such as those named and described in Chapter 25, p. 287, of "Rocket Propellant Handbook," by B. Kit and D. S. Evered, published by the Macmillan Co., New York, 1960. All such polymeric organic binders are characterized by a relatively high fuel value which requires a large proportion of inorganic oxidizing agent for development of the maximum amount of energy. Thus, the inorganic oxidizer may comprise 75 to 85% and even more of the weight of the composite propellant, and other additives about 5%, leaving only 10 to 20% of the composition as binder. The relatively small proportion of binder which is permitted in a composite composition designed for maximum propellant effectiveness may cause formulation problems and often leads to marginal physical properties in the finished composition.

Attempts have been made to increase the effectiveness of a polymeric organic binder as a matrix forming material by including in the total composition components which act as plasticizer for the polymeric material and thereby improve the ease both of mixing and of shaping the total propellant composition. However, since such plasticizers also generally are organic materials of high fuel value, their inclusion does not permit a significant reduction in the proportion of granular solid oxidizer to be incorporated in the composition, and hence does not convey a maximum improvement in the processing and performance characteristics of the composition.

Polyurethanes are recognized as desirable binders because of their good physical properties and the valuable properties which they confer on composite propellants formulated with them. The polyurethanes, however, suffer from the drawback mentioned above, viz., the high requirement of solid oxidizer to be used with them. For these, as for most other polymeric binders, there is need for a means of reducing the proportion of solid oxidizer which often contributes friability to the finished polyurethane-containing composition and excludes the possibility of incorporating high energy additive fuels such as finely divided metals of low atomic number.

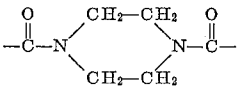
Incorporation of an energy-rich, fluid, oxygen-bearing plasticizer in the polyurethane binder composition offers a means of overcoming the difficulties described above. Since such a plasticizer requires no inorganic oxidizer and, in fact, itself contributes oxygen to the mixture, a corresponding reduction in the proportion of solid inorganic oxidizer in the composition is practicable. The resulting increased proportion of binder matrix increases the flexibility and toughness of propellant grains without destroying the essential fuel-oxidizer balance that produces the maximum effective impulse during the combustion which occurs upon firing the propellant composition in a rocket.

An additional benefit can be realized by use of an effective oxidizing plasticizer in the binder composition. If, in contrast to the condition described above, additional binder matrix is not required in the composite propellant, the displaced solid inorganic oxidizer may be replaced by a suitably balanced blend of an inorganic oxidizer and a fuel additive such as a finely divided metal from the group comprising boron, aluminum, and magnesium, of which aluminum especially is preferred. The high heat of combustion of the metal, say aluminum, further increases both the specific impulse and the density impulse of the propellant composition beyond that attainable in the absence of the metal fuel additive.

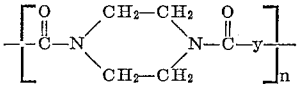
Nitroglycerin for many years has been used as a component of conventional double base propellants, i.e., those containing principally nitrocellulose and nitroglycerin. Nitroglycerin is an effective energy-rich plasticizer for

nitrocellulose and is especially valuable because of its high density and also because it is an oxygen-rich plasticizer. Attempts have been made to incorporate nitroglycerin into other polymeric organic binders, but generally with little or only limited success because the nitroglycerin is poorly compatible and sooner or later gradually exudes from the composition, thereby resulting in changes in the composition and in the properties and performance of the propellant, and additionally creates a relatively hazardous condition due to localized accumulations of nitroglycerin.

In accordance with this invention, the difficulties encountered heretofore can be overcome by preparing as a binder for a composite propellant a plasticized mixture of nitroglycerin and a thermoplastic elastic copolymer consisting essentially of the recurring units (a) —O—G—O—, (b) O—X—O, and (c) —Y— connected by the bivalent acyl radical



wherein —O—G—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a polymeric glycol having a molecular weight of at least 800 and selected from the group consisting of polyalkyleneether glycols and polyester glycols; —O—X—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a glycol having a molecular weight of less than 250; and —Y— is a bivalent hydrocarbon radical having a molecular weight of less than 200 and selected so that the polypiperazine amide, having repeating units of the structure



in the fiber-forming molecular weight range melts above 200° C.; said recurring units (a), (b), and (c) being present in amounts such that the molar ratios of $a:b:c$ are 1.0:0.0–3.0:0.0–2.0 and the sum of $b+2c$ is equal to or greater than 2. Thermoplastic elastic copolymers of the kind defined above contain a multiplicity of urethane structural units and hence fall within the general category of modified polyurethanes, and are further characterized by a high degree of compatibility with nitroglycerin. That is, the polymer is solvated by the nitroglycerin plasticizer to form a solidified or semi-solidified composition from which the nitroglycerin is not lost by exudation even after long storage at elevated temperatures.

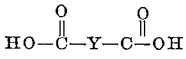
In compositions of the instant invention, the G in the recurring (a) units is derived from glycols which may be represented by the general formula HOGOH and have a molecular weight of at least 800. Useful polyalkyleneether glycols are represented by the formula $HO(RO)_nH$ wherein R is an alkylene radical containing up to 10 carbon atoms and n is an integer such that the molecular weight of the polyalkyleneether glycol is at least 800. Representative examples of these glycols are poly-1,2-propyleneether glycol, ethylene oxide modified polypropyleneether glycol, polytetramethylene ether glycol and polytetramethylene formal glycol. Of these glycols polytetramethyleneether glycol of 800–3500 number average molecular weight is preferred. The polyalkyleneether glycols are made by the polymerization of cyclic ethers such as ethylene oxide, propylene oxides and tetrahydrofuran or by condensation of low molecular weight glycols.

The polyester glycols which are useful in the present invention have an acid number of less than 2 and a number average molecular weight of at least 800. They may be prepared by condensation polymerization of a dicarboxylic acid with more than one mole of an organic diol. The excess of diol determines the molecular weight of the polyester glycol produced. Representative examples

of diols which may be used to prepare polyester glycols for use in the present invention include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, thiodiglycol, diethylene glycol and triethylene glycol. Aliphatic dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, sebacic acid, and maleic acid, are generally preferred, but small amounts of aromatic dicarboxylic acids such as phthalic acid and terephthalic acid may also be used. Anhydrides of dicarboxylic acids may be conveniently employed in place of the acids when they are available.

The X in —O—X—O (unit (b) above) is a bivalent radical obtained by removing the hydroxyl groups from a glycol having a molecular weight of less than 250 and a general formula of H—O—X—O—H. Representative glycols include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, thiodiglycol, diethylene glycol, 2,2-dimethylpropanediol-1,3, 2-methyl-2-ethylpropanediol-1,3, cyclohexanediol-1,4, 1,4-dihydroxymethylbenzene, 1,4-dihydroxymethylcyclohexane, 1,5-pentanediol and 1,10-decanediol.

The —Y— in unit (c) above is a bivalent hydrocarbon radical having a molecular weight of less than 250 which may be considered as being derived from a dicarboxylic acid having the structure



Representative dicarboxylic acids include succinic acid, glutaric acid, adipic acid, suberic acid, terephthalic acid, maleic acid and cyclohexane-1,4-dicarboxylic acid.

By nitroglycerin is meant the explosive liquid nitrate ester, glycerol trinitrate, and also the various mixtures of glycerol trinitrate and other nitrate esters such as ethylene glycol dinitrate commonly employed in the explosive industry.

Oxidizers suitable for use in composite propellants of the instant invention include lithium perchlorate, sodium perchlorate, potassium perchlorate, ammonium perchlorate, ammonium nitrate, sodium nitrate, and potassium nitrate, the perchlorates—especially ammonium perchlorate—being preferred.

Fuels in addition to the plasticized binder, sometimes designated as fuel additives, may be included in said composite propellants. Suitable fuels include finely divided metals, especially those of lower atomic number such as aluminum, magnesium and boron; carbon; and metal hydrides such as lithium aluminum hydride.

Minor amounts of other additives such as stabilizers, antacids, catalysts, and the like also may be included in composite propellants of the present invention.

It is to be understood that each of the various types of compounding ingredients can be used singly, or mixtures of various ingredients performing a certain function can be employed.

The following examples are illustrative of the invention, but are not to be regarded as limiting the scope of the invention in any way. In the examples, parts are by weight unless otherwise indicated.

Example 1

This example illustrates the preparation of a thermoplastic elastic copolymer suitable for use in the instant invention.

A mixture of 500 parts of polytetramethyleneether glycol having an average molecular weight of about 1000 and 90 parts of 1,4-butanediol is added dropwise to 1400 parts of liquified phosgene, and held under reflux for 12 hours. At the end of this time, the excess phosgene is removed by passing a rapid flow of nitrogen gas through the reaction mixture.

The above phosgenation product (50 parts) and 5.8 parts of adipoyl chloride is added rapidly to a solution of 11.7 parts of piperazine in 540 parts of methylene chloride. The mixture is stirred in a blender at high

speed for one minute and then 200 parts of 10% aqueous sodium carbonate solution is added, and agitation is continued for 20 minutes. About 0.6 part of N,N'-di-β-naphthyl-p-phenylene diamine is added as antioxidant and stabilizer and mixed into the reaction mass. The resulting thick emulsion is poured into boiling water to volatilize and remove the methylene chloride. The insoluble polymer separates as a finely divided material which is washed with fresh water, and dried.

The thermoplastic elastic copolymer prepared in this way has an inherent viscosity of about 2.5 in m-cresol solution. The copolymer may be press-molded into a sheet or other shape at about 225° C. and 500 p.s.i.g. pressure, with cooling of the mold to a temperature below 150° C. before pressure is released. The copolymer also may be injection molded. Using conventional equipment, the solid molded copolymer is cut into particles of controlled size which may be preferred for the formulation of composite propellant compositions.

Example 2

This example illustrates formation of a nitroglycerin-plasticized binder composition of the instant invention.

Two equal portions of the dried thermoplastic elastic copolymer of Example 1 in finely divided form were mixed separately at ambient room temperature with 1½ times and 2 times their weight, respectively, of nitroglycerin. In each instance, the nitroglycerin was absorbed rapidly by the copolymer giving a non-flowable composition. After three days of storage at room temperature, the mixtures were essentially homogeneous and form-stable, and were less tough than a corresponding nitrocellulose-nitroglycerin composition.

Absorption of nitroglycerin occurred much less rapidly when the thermoplastic elastic copolymer was in a more massive form. Thus, two samples of press-molded copolymer of Example 1 in the form of chips about 1 inch square and 1/16 inch thick were immersed in nitroglycerin at about 25° C. for six days. The gain in weight, i.e., nitroglycerin absorbed, is shown in the tabulation below.

Time	Percent Weight Increase	
	Sample 1	Sample 2
24 hours	47	52
28 hours	73	73
72 hours	90	86
144 hours	141	140

The above data emphasize the importance of particle size of the copolymer in controlling the rate of absorption of nitroglycerin. In 6 days the large chips absorbed less nitroglycerin than was absorbed almost at once by the same copolymer in finely divided form. The average degree of polymerization as characterized by the inherent viscosity also is a factor which influences the rate of absorption of nitroglycerin to form a nitroglycerin-plasticized copolymer of the instant invention. In general, the particle size of the binder will range from 50 microns to 1000 microns, material of 200 to 500 microns being preferred. The inherent viscosity of the copolymers in m-cresol will range from 1.7 to 6.0 (believed to correspond to molecular weights of 50,000–200,000), with an indicated preference for copolymers having inherents in the range of 2.0 or more.

Example 3

A composite propellant composition is made by blending 18.4 parts of granular thermoplastic elastic copolymer, prepared as in Example 1, with 63.2 parts of granular ammonium perchlorate. The blend then is mixed with 18.4 parts of liquid nitroglycerin. The resulting composition has a calculated specific impulse of 244 lb. sec./lb. (shifting equilibrium, 1000 p.s.i. to 1 atms.), and a corresponding density impulse of 397 sec./cc. (density impulse is the product of density and specific impulse).

The specific impulse values in this and the subsequent example are based on the most recent Joint Army-Navy-Air Force thermodynamic data.

Example 4

A composite propellant containing finely divided aluminum as a fuel additive is formulated to have the following composition:

Ingredient:	Percent
Ammonium perchlorate	69.3
Thermoplastic elastic copolymer (Ex. 1)	5.0
Aluminum powder	20.7
Nitroglycerin	5.0
	100.0

The resulting propellant composition has a calculated specific impulse of 259 lb. sec./lb. (shifting equilibrium), and a corresponding density impulse of 506 g. sec./cc.

The gain in specific impulse which results by including the aluminum fuel additive is apparent. The effectiveness of the NG plasticized-thermoplastic elastic copolymer binder of the instant invention facilitates the formulation of such higher specific impulse propellants.

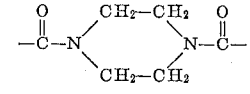
It will be understood that numerous changes and modifications may be made in the subject matter described above without departing from the scope of the invention as defined in the appended claims.

What is claimed is:

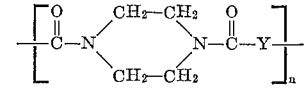
1. A composition of matter comprising a mixture of nitroglycerin and a thermoplastic elastic copolymer consisting essentially of the recurring units

(a) —O—G—O—, (b) —O—X—O, and (c) —Y—

connected by the bivalent acyl radical



wherein —O—G—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a polymeric glycol having a molecular weight of at least 800 and selected from the group consisting of polyalkyleneether glycols and polyester glycols; —O—X—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a glycol having a molecular weight of less than 250; and —Y— is a bivalent hydrocarbon radical having a molecular weight of less than 200 and selected so that the polypiperazine amide, having repeating units of the structure

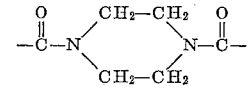


in the fiber-forming molecular weight range, melts above 200° C.; said recurring units (a), (b), and (c) being present in amounts such that the molar ratios of $a:b:c$ are 1.0:0.0–3.0:0.0–2.0 and the sum of $b+2c$ is equal or greater than 2.

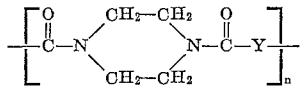
2. A propellant composition comprising 50 to 90 weight percent of a solid inorganic oxidizer and from 10 to 50 weight percent of a binder consisting essentially of a mixture of 10 to 70% by weight of nitroglycerin and 30 to 90% by weight of a thermoplastic elastic copolymer consisting essentially of the recurring units

(a) —O—G—O—, (b) —O—X—O, and (c) —Y—

connected by the bivalent acyl radical



wherein —O—G—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a polymeric glycol having a molecular weight of at least 800 and selected from the group consisting of polyalkyleneether glycols and polyester glycols; —O—X—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a glycol having a molecular weight of less than 250; and —Y— is a bivalent hydrocarbon radical having a molecular weight of less than 200 and selected so that the polypiperazine amide, having repeating units of the structure

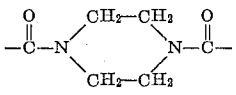


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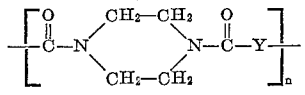
3. A propellant composition comprising 50 to 90 weight percent of a solid inorganic oxidizer, 20 to 35 weight percent of a finely divided metal, and 10 to 30 weight percent of a binder consisting essentially of a mixture of 10 to 70% by weight of nitroglycerin and 30 to 90% by weight of a thermoplastic elastic copolymer consisting essentially of the recurring units

(a) —O—G—O—, (b) —O—X—O, and (c) —Y—

connected by the bivalent acyl radical



wherein —O—G—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a polymeric glycol having a molecular weight of at least 800 and selected from the group consisting of polyalkyleneether glycols and polyester glycols; —O—X—O is a bivalent radical obtained by removing the hydroxyl hydrogen atoms from a glycol having a molecular weight of less than 200 and —Y— is a bivalent hydrocarbon radical having a molecular weight of less than 200 and selected so that the polypiperazine amide, having repeating units of the structure



in the fiber-forming molecular weight range, melts above 200° C.; said recurring units (a), (b), and (c) being present in amounts such that the molar ratios of $a:b:c$ are 1.0:0.0–3.0:0.0–2.0 and the sum of $b+2c$ is equal to or greater than 2.

4. A process for the preparation of the composition described in claim **1** wherein the thermoplastic elastic copolymer in the form of fine granules is mixed with nitroglycerin at room temperature, the mixture is cast into a mold, and the mixture in the mold is heated until plasticization, gelation, and solidification occur.

5. A process for preparation of the composition described in claim **2** wherein an intimate mixture of solid inorganic oxidizer and fine granules of thermoplastic elastic copolymer is mixed with nitroglycerin, the resulting mixture is cast into a mold, and the charged mold is heated until plasticization, gelation, and solidification occur.

6. A process for preparation of the composition described in claim **3** wherein an intimate mixture of solid inorganic oxidizer, fine granules of the thermoplastic elastic copolymer, and a finely divided metal is mixed with nitroglycerin, the resulting mixture is cast into a mold, and the charged mold is heated until plasticization, gelation, and solidification occur.

No references cited.

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