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THIXOTROPIC PROPELLANT

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to propellants, that is, safe sources of hot gases which may be used for the propulsion of projectiles such as missiles, rockets and torpedoes and any other vehicle which cannot use air as a source of oxidizer. Specifically, the invention relates to a liquid propellant which utilizes a thixotropic material as a suspending medium.

In the present state of the art, propellants are generally divided into two classes—solid and liquid. Solid propellants are based on (1) nitrocellulose which has been plasticized with nitroglycerin and/or other explosive or non-explosive plasticizer plus additives to increase storage life, burning characteristics, mechanical strength and toughness and (2) resinous binders which also act as fuels and which contain a high concentration (65%–85%) of inorganic oxidizer, such as perchlorates and nitrates, as filler, plus burning catalysts and other additives. Solid propellants are advantageous in that they are safely and easily stored and transported and require little or no machinery in the vehicle. They have the disadvantages, however, of providing no means of programming fuel consumption rate other than by grain design, of being expensive and difficult to process, in not allowing for changes in burning and mechanical properties as a function of propellant temperatures and of being dangerous in regard to the possibility of the burning changing from combustion to explosion.

Liquid propellants are, generally, of two types—monopropellants and bipropellants. The monopropellants are characterized by a single phase containing both fuel and oxidant, combined or mixed. The monopropellant may comprise a single material which has both fuel and oxidant present in the same molecule or it may comprise a mixture of fuel and oxidant. Either type of monopropellant may contain other materials which contribute to the overall efficiency of the system. Typical monopropellants which contain both fuel and oxidant in the same molecule are hydrazine and diethylene glycol. Typical monopropellant systems which are composed of a mixture of fuel and oxidant are aniline-nitric acid, hydrazine-liquid oxygen and ammonia-liquid oxygen.

The liquid propellants are desirable because they are readily adapted to controlled fuel consumption rate during flight, thus allowing for programming. Moreover, a minimum of processing is necessary and the liquid propellants allow the use of relatively small burning chambers which are necessary for high pressure operation and improved thermodynamics. Liquid propellants are, however, disadvantageous in that they require (1) the use of pumps and meters whose operating characteristics must be carefully balanced for efficient operation, and (2) the need for storage and transportation of extremely corrosive and explosive liquids such as nitric acid and liquid oxygen.

At the present time there is under development a slurry monopropellant in which a solid explosive or oxidizer is suspended in a desensitized liquid explosive. This system is advantageous in that it (1) requires only one set of metering machinery instead of two, (2) is easily stored

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and transported and (3) possesses all other advantages of liquid systems as set forth above. This type of propellant is disadvantageous in that there is only a limited number of mixtures which may be used since (1) the solid must be insoluble in the liquid, (2) the solid must have the same specific gravity as the liquid, and (3) the temperature coefficient of volumetric expansion of the liquid will usually be larger than that of the solid. This material must be stored, shipped and used over a very narrow temperature range since it is otherwise impossible to maintain homogeneity of composition. Lack of homogeneity of composition deleteriously affects the safety, burning and other properties of the material.

A further advance in the art has become apparent recently by the use of gelatin monopropellants which combine many of the advantages and eliminate many of the disadvantages of solid and liquid propellants. These gelatin monopropellants comprise a dispersion of a solid oxidizer in a matrix of liquid fuel to which a gelling agent has been added. The gelling agents which are added are, among others, organic materials such as polyvinyl chloride, ethyl cellulose, polyvinyl acetate and metal salts of higher fatty acids. Further, certain monopropellants such as hydrazine and ethylene oxide act like water in the presence of hydrophilic sols such as gum tragacanth and sodium alginate and can be gelled by the addition thereto of small amounts of such materials. Even in the light of these recent advances, however, the fuel and the gelling agent must be carefully matched in order to obtain maximum benefit therefrom. Unless the fuel and gelling agent are carefully matched, the gel is unstable and its stiffness is difficult to control. Moreover, the addition of an undesirable gelling agent to a fuel may seriously affect the oxygen balance of the fuel and impair other properties.

In spite of the difficulties and complexities presented by the art, it has now been found that it is possible to prepare propellants having infinite viscosities and that solid components may be added thereto and suspended therein without regard to the respective specific gravities of the liquid propellant and the suspended solids.

The propellant compositions of this invention are prepared by a novel method which comprises rendering a liquid propellant thixotropic and suspending therein whatever materials, such as oxidizers, fuels, catalysts and other additives, as are desired.

Thixotropy may be induced in many ways and the gel obtained is capable of preventing the fuel from "bleeding" out of the mixture and the solid additives from settling to the bottom. Moreover, the thixotropic mixture may be pumped and metered in the same fashion as non-thixotropic liquid propellants.

In accordance with the method of the present invention, thixotropy of liquid propellants is obtained by the addition thereto of very finely divided particulate material having a particle size range of from less than 1 to about 20 millimicrons and in a concentration of from about 1 to about 5 percent by weight of the propellant, the concentration varying approximately inversely with the dielectric constant of the liquid.

As finely divided particulate material there may be used silica or any particulate form of carbon such as the various carbon blacks, graphite, coal, coke, channel blacks, thermal blacks, furnace blacks, acetylene black, etc. Moreover, finely divided metals may also be used, such as powdered aluminum, magnesium and boron.

The addition of the particulate material described above and similar materials to a liquid will result in the mixture having, at the same temperature and pressure, viscosities over an 80-fold range. The significance of such a wide viscosity range is that anything which is chemically compatible and insoluble in such a mixture

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of liquid and fine, particulate material can be suspended therein and yet the mixture will exhibit flow characteristics under the proper shearing force.

The following examples illustrate specific embodiments of the invention but it is to be understood that the particular systems illustrated are not and should not be construed as a limitation of the scope of the invention.

Example I

A mixture containing 53.5 wt. percent nitroglycerin and 22.9 wt. percent triacetin was prepared. To the mixture was added 3.6 wt. percent silica having an average particle size of about 1-20 millimicrons. To the gel obtained, there was added, with stirring and at ambient temperature and pressure, 20 wt. percent ammonium nitrate.

The specific gravity of the liquid was 1.42 and the specific gravity of the suspended solids was 2.3. No sign of setting was apparent in this material after storage for 7 days over a thirty degree centigrade temperature range.

Example II

To the initial gel obtained in Example I was added 16 wt. percent ammonium nitrate and 4 wt. percent CaB_6 .

The specific gravity of the liquid was 1.42 and the specific gravity of the suspended solids was 1.72. Again, no sign of settling was apparent after 7 days' storage over a thirty degree centigrade temperature range.

The suspensions, as illustrated in Examples I and II, have viscosities in the range of 200-8000 poises.

The invention encompasses, of course, not merely thixotropic monopropellants but also bipropellants in which it is desirable to suspend solids in the liquid fuel in order to alter the burning characteristics, increase the specific impulse of the system or otherwise modify performance.

A comprehensive grouping of monopropellants, which contain both fuel and oxidant in the same molecule and which may be used in lieu of nitroglycerin, as illustrated by the examples, includes hydrogen peroxide, ethylene oxide and propylene oxide and mixtures thereof, hydrazines, alkyl nitrates such as propyl nitrate, glycols such as diethylene and triethylene glycols, nitroparaffins such as nitromethane, nitroethane, nitropropane and nitrobutane, alcohols such as methyl and ethyl alcohol and mixtures thereof, isopropyl alcohol and ethyl silicate.

An illustrative grouping of monopropellants which comprise a mixture of fuel and oxidant, and which may be substituted for the monopropellants of the examples, includes, as fuels, acetylene, methyl acetylene, ammonia, aniline, ethylamine, methylamine, ethylene diamine, o-toluidine, triethyl amine, hydrazine, unsymmetrical dimethyl hydrazine, dimethylenetriamine, alkanes such as methane, ethane, heptane and dodecane, methyl o-naphthyl ether, benzyl alcohol, furfuryl alcohol, benzene, xylidene, triethyl benzene, methyl cyclopentane, turpentine, kerosene, gasoline, hydrogen, methyl maleate, diethyl phthalate, butyl oxalate, ethylene, methylal, lithium, lithium hydride, aluminum borohydride, diborane, butyl mercaptan, triethyl trithiophosphite and trimethyl trithiophosphite. Oxidizers which may be used include chlorine, fluorine, chlorine trifluoride, perchloryl fluoride, nitrogen fluoride, chlorine heptoxide and tetroxide, hydrogen peroxide, mixtures of ammonium nitrate, hydrogen peroxide and water, nitric acid and its red and white fuming varieties, potassium permanganate, nitrogen tetroxide, oxygen, ozone, oxygen difluoride, tetranitromethane, the alkali metal nitrates and perchlorates, barium peroxide and finely divided metal powders such as aluminum, magnesium and boron.

The solids which are added to the liquid mono- and bipropellant systems contemplated herein may be combustible solids such as oxidizers or noncombustible solids such as burning rate catalysts and other materials such as metal powders designed to affect the burning characteris-

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tics and power of the system. Such combustible and non-combustible solids are uniformly dispersed throughout the liquid and suspended therein by the gel-like structure of the system when at rest. The concentration of solid oxidizer, etc. has no discernable effect on the gelling and flow characteristics of the system, however, such characteristics being primarily determined by the concentration of finely divided, particulate material which has been incorporated into the system.

Desensitizers, such as triacetin, are added to the nitroglycerin in order to render it safe to handle. Other compounds which may be used in place of triacetin are the dialkyl phthalates, tripropanoin and tributyrin. In fact, any low vapor pressure, soluble, chemically compatible organic material may be used as the desensitizer.

Other additives, whether solid or liquid, may be added to the propellants contemplated by this invention in accordance with the procedures set forth hereinabove.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Having thus described the invention, what is claimed and desired to be secured by Letters Patent of the United States is:

1. In a propellant composition comprising a liquid fuel component, a solid component selected from the group consisting of oxidizers, burning rate catalysts, fuels, and mixtures thereof the improvement which comprises a finely divided particulate material uniformly dispersed in said liquid component as the sole component for rendering the composition thixotropic, said particulate material having a particle size less than about 20 millimicrons and being selected from the group consisting of silica, carbon, and finely divided metals.

2. The composition of claim 1 wherein said particulate material is present in a concentration of 1-5 weight percent based on the liquid component.

3. The composition of claim 1 further including a liquid oxidizer component.

4. The composition of claim 1 wherein said liquid fuel component is nitroglycerin, said solid component is ammonium nitrate and said particulate material is silica.

5. The composition of claim 1 wherein said particulate material is silica.

6. The composition of claim 1 wherein said particulate material is carbon.

7. The method of forming a thixotropic propellant composition which comprises:

(a) incorporating a particulate material having a particle size of less than about 20 millimicrons in a liquid fuel so as to form a first mixture, said particulate material being the sole component for rendering the composition thixotropic and being selected from the group consisting of silica, carbon and finely divided metals;

(b) allowing said first mixture to gel; and

(c) incorporating a solid component selected from the group consisting of oxidizers, burning rate catalysts, metal powders and mixtures thereof in said gel to form a second mixture and allowing said second mixture to gel.

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