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SOLID HYDROCARBON RESIN ROCKET PROPELLANTS AND METHOD OF PROPULSION

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The present invention relates to a rocket propellant composition and to the use of petroleum resins as binders therein. More specifically, it concerns the use of small amounts, i.e. 10 wt. percent or less, of resin obtained from steam-cracked petroleum in high energy solid propellants.

Heretofore, binders having low fuel value, such as natural rubber, polyisobutylene, polyurethane, etc., have been used to hold solid fuels and oxidizers together. However, the binders known in the art do not impart the necessary strength to the finished propellant unless excessive amounts of them are employed, e.g. 10 or 20 wt. percent. The maximum quantity of low fuel value binder that can be tolerated in high energy propellants, i.e. those having specific impulses greater than 250 sec.$^{-1}$, is usually not more than 10 wt. percent and preferably not more than 5 wt. percent.

The object of this invention is to provide a rocket propellant that has good tensile and compressive strengths yet contains no more than 10 wt. percent of a low fuel value binder.

In accordance with the present invention small amounts of hydrocarbon resins are used as binders in high energy rocket propellants. While up to 10 wt. percent of these resins may be employed, it has been found that substantially less than this amount is highly satisfactory. The resins of the present invention are unique in that they impart tensile strengths of more than 100 p.s.i. even when used in very low concentrations, e.g. 2.5 wt. percent while other polymeric binders do not provide such strength when employed in such amounts. This surprising property allows the rocket propellant formulator to take full advantage of the high energy fuels and oxidizers which he intends to use in a given propellant.

The concentration of binder in the propellant can be highly critical especially where the desired impulse is close to the actual impulse of the propellant. Generally speaking, approximately 2 units of impulse are lost per 1 wt. percent of low fuel value binder employed. In other words, if it is necessary to use 15 wt. percent of a conventional binder in order to impart the minimum strength, i.e. about 100 p.s.i., which is thought to be necessary to prevent cracking during the burning stage, as much as 20 additional units of impulse or more can be obtained by substituting 5 wt. percent of the hydrocarbon resins described herein.

The binder of the present invention has special application to high energy nonhypergolic solid rocket propellants in which highly reactive fuels and oxidizing agents are present. The solid fuel and solid oxidizer, or the fuel alone where it is a monopropellant, is admixed with small amounts of the resin binder usually in the presence of a low boiling inert liquid solvent such as a C_5 to C_8 hydrocarbon for from a few seconds to 10 or 15 minutes at room temperature or lower, e.g. 10° C. It is sometimes advantageous to premix the fuel and oxidizer for a short period at room temperature in order to insure a homogeneous propellant. The resin is then added to the premix as a 5 to 80 wt. percent solution in, for instance, n-pentane. If desired, the resin can be added in small portions to the propellant mixture. Care should be taken not to whip air into the mixture because a large number of voids

leads to uneven burning. After the resin has been thoroughly admixed with the fuel and oxidizer, the diluent is removed by heating the mixture or by reducing the pressure below atmospheric pressure, e.g. 10 to 600 mm., or both. The actual density of the final mixture should be at least 99% of the theoretical density. Of course, higher temperatures, e.g. up to 200° C., may be used if the fuel and oxidizer are stable at such temperatures. In such a case, the resin may be added in a melted form and thus the need for a solvent is eliminated. The mixture is then molded, usually under pressure, into the desired form.

The liquid solvent used in the above-described process may be a paraffinic or olefinic, cyclic or acyclic hydrocarbon. Suitable solvents include n-hexane, benzene, n-octane, cyclohexane and xylene. Halogenated C_1 to C_6 hydrocarbons, such as carbon tetrachloride and ethylene dichloride may also be employed. The type of solvent is not critical and the only requirements are that it have a substantial affinity for the resin and be inert so that the fuel and oxidizer are not adversely affected.

The fuel and oxidizer should be small, discrete particles which can be admixed to form a homogeneous mixture, i.e. one having substantially the same composition throughout. In general, the particle sizes are between about 1 and 250 microns in diameter, with sizes of 5 to 100 microns being preferred. Any conventional solid fuel and oxidizer may be used. Suitable fuels include the metals of Groups I, II and III of the Periodic Chart of Elements shown on pages 56 and 57 of Lange's Handbook of Chemistry, 8th edition, as well as their hydrides. The preferred inorganic fuels are substances containing metals of Groups II–A and III–A (including boron). Among the metals which can be used as fuels are lithium, cesium, aluminum, beryllium, boron and magnesium. Nitrogen fuels, such as hydrazine diborane and hydrazine monoborane, may also be used. Solid inorganic and organic oxidizing agents that can be employed in the manufacture of this novel rocket composition include ammonium perchlorate, lithium perchlorate, sodium perchlorate, nitrocellulose, hexanitroethane and sodium nitrate. These oxidizers are characterized by the fact that they all contain oxygen or nitrogen-oxygen groups. The particular oxidizer-fuel mixture selected for a propellant system should be relatively stable so that no explosion takes place while it is being prepared.

The hydrocarbon resins employed in the rocket propellant system of the present invention are prepared from cracked petroleum distillates boiling in the range of about 20° to 280° C. including any fractions boiling within this range. The aforementioned distillates comprise a mixture of olefinic and paraffinic hydrocarbons, the former being the major component. In general, these distillates have a carbon number range of 5 to 9 and contain about 30 to 68 wt. percent monoolefins, 8 to 24 wt. percent diolefins, 19 to 45 wt. percent aromatics and 1 to 5 wt. percent paraffins and naphthenes. Such distillates are obtained by cracking kerosene, gas oil, naphtha or petrolatum in the presence of 50 to 90 mole percent steam at temperatures of about 540 to 870° C.

The selected fractions are polymerized by contacting it with a Friedel-Crafts catalyst, usually a halide such as aluminum chloride or boron fluoride, at temperatures of —30 to 75° C. for from a few minutes to an hour or more under substantially atmospheric pressure. Upon completion of the polymerization, any excess catalyst may be quenched by any of the methods well known in the art, such as the addition of methyl alcohol followed by filtration and washing with dilute acid, caustic and/or water.

Optionally, the steam-cracked hydrocarbon fraction

may be modified prior to polymerization by dimerizing the cyclodienes in the fraction, notably cyclopentadiene methyl cyclopentadiene, by subjecting the fraction, e.g. 70° to 130° C., to temperatures of 90° to 140° C. for about 1 to 8 hours. On the other hand, it is sometimes desirable to add about 5 to 20 wt. percent of said cyclodienes to the fraction before polymerizing it. Also, the cyclodienes or divinylbenzene may be added to the resin and reacted therewith to improve its softening point.

The resins, which are thermoplastic, usually have softening points between about 50° and 110° C. and average molecular weights of about 1000 to 5000, preferably not above 2000. They are essentially alkylated paraffin chains containing a small amount of unsaturation, generally about 2 double bonds per molecule. Their specific gravities may range from 0.96 up to 0.98.

The propellant containing the resin may be molded under 500 to 30,000 pounds pressure into any desired form, such as star-shaped or cylindrical, and in some instances a mandrel may be used to provide the propellant with a hollow core which may be round or otherwise. The various shapes and forms of the propellant grain are arbitrary insofar as the invention is concerned since a solid cylinder which burns like a cigarette is adequate.

The amount of fuel and oxidizer used in a given propellant will vary according to the specific impulse wanted, the particular fuel and oxidizer selected and other things. Some of the high energy propellants contain from 5 up to 40 wt. percent of fuel, although about 10 to 30 wt. percent fuel is most commonly used. The oxidizer comprises the balance of the formulation after the amount for the binder has been taken into consideration. In many propellants, the oxidizer may compose as much as 80 wt. percent or as little as 25 wt. percent of the total composition. Preferably, the propellant contains about 35 to 80 wt. percent oxidizer, 10 to 30 wt. percent fuel and 1 to 5 wt. percent resin.

The propellants of the present invention may be placed in the combustion zone of a pure rocket device and ignited by a suitable means, such as an electric match to impart thrust to the rocket. The propellant is highly resistant to fracturing and disintegration due to its strength.

The invention is described in detail in the following examples in order to permit a fuller understanding of it.

EXAMPLE 1

A steam-cracked petroleum resin having a softening point (Ring and Ball Method) of 100° C., an average molecular weight of 1500 and a specific gravity of 0.96 was prepared by polymerizing a feed consisting of a hydrocarbon fraction boiling between 20° and 140° C. with 1 wt. percent aluminum chloride at 20° C., is used to prepare a rocket propellant composition. The aforementioned feed contains about 50 wt. percent acyclic and cyclic monoolefins comprising pentenes, hexenes, heptenes and octenes; about 15 wt. percent acyclic and cyclic diolefins comprising cyclopentadiene, piperylene, etc.; about 30 wt. percent aromatics comprising benzene, toluene and xylenes; and about 5 wt. percent paraffins and naphthenes. The resin is dissolved in 50 wt. percent n-pentane and 5 parts by weight of resin is added to 31.9 parts by weight of ammonium perchlorate, 13.1 parts by weight of powdered aluminum (ca. 100 microns) and 50 parts by weight of hydrazine diborane which had been premixed for 5 minutes. The resin solution is added slowly with mixing. Thereafter the propellant composition is mixed until a total mixing time of 30 minutes has elapsed. The resulting homogeneous mixture is subjected to reduced pressure, i.e. 50 mm. of mercury absolute pressure, for 3 hours to remove the pentane solvent. The stripped composition is then placed in a 2 cc. mold and subjected to 20,000 p.s.i.g. pressure for 15 minutes. The resulting propellant composition is a rigid solid having a tensile strength in excess of 500 p.s.i., a compressive strength of about 20,000 pounds, and a calculated specific impulse of 284 sec.$^{-1}$ under 1000 p.s.i.

The tensile strength of the finished propellant is measured as follows: bars one inch long and ¼-inch wide and high are molded in a remotely operated compression mold under 20,000 p.s.i.g. pressure. Each bar is then broken, also remotely, by supporting it at the ends and loading it in the middle. The load is continually increased until the bar fails, and the failure load is recorded. The modulus of rupture is defined as follows:

$$\text{Modulus of rupture, p.s.i.} = 3Wl/2bd^2$$

where

W=maximum load, lbs.
l=length of span, inches
b=width of bar, inches
d=depth of bar, inches.

For brittle materials, i.e. those which do not deform appreciably before breaking, the modulus of rupture is identical to the tensile strength.

Burning studies conducted with the above propellant show that it burns regularly at the rate of 1.61 inches per sec. under 1000 p.s.i. while a similar propellant containing no resin binder burned irregularly because the propellant broke up while it was burning.

EXAMPLE 2

Example 1 is repeated except that 2.5 wt. percent of the resin is added to the propellant mix which also contains 60 wt. percent of hydrazine diborane, 12.25 wt. percent aluminum and 25.25 wt. percent ammonium perchlorate. The specific impulse at 1000 p.s.i. is calculated as being 290 sec.$^{-1}$. The tensile strength of the propellant is more than 500 p.s.i. and compressive strength is over 6000 lbs. The latter property is measured in a Marshall Tester at room temperature with a cylindrical sample that is 5 inches high and 4 inches in diameter.

In order to demonstrate the unique properties of petroleum steam-cracked resins as binders in rocket propellants, a number of other substances were evaluated together with the above-described resin in a comparative study. The prototype system consists of sodium chloride and aluminum powder in a weight ratio of 5.3:1, the binder being the balance of the formula. The systems are compounded as described in Example 1. The results are set forth in the table:

Binder	Tensile Strength, p.s.i. (2.5 Wt. Percent Binder)	Tensile Strength, p.s.i. (5 Wt. Percent Binder)
Steam-cracked resin (MW 1500)	130	240
Polyethylene (MW 5000)	50	50
Butadiene-styrene copolymer* (MW 1000)	30	30
Polyisobutylene (MW 1000)	15	30

*80 wt. percent butadiene and 20 wt. percent styrene.

The data show that the steam-cracked petroleum resin is suitable and far superior to other resins even when used in small amounts, e.g. 2.5 wt. percent.

The tensile strength of these samples were measured with the Scott Instron using a dumbbell-shaped sample which is ½-inch thick and ½-inch wide at the narrowest point.

It is not intended to restrict the present invention to the foregoing examples which are merely given to demonstrate some of the embodiments of the invention. It should only be limited to the appended claims in which it is intended to claim all of the novelty inherent in the invention as well as the modifications and equivalents coming within the scope and spirit of the invention.

What is claimed is:

1. A solid rocket propellant consisting essentially of high-energy propellant solid particles held together in a solid composite by a binder which is 1 to 10 wt. percent

of the composite, said binder being a hydrocarbon resin made by polymerizing with a Friedel-Crafts catalyst a steam-cracked petroleum fraction boiling in the range of 20° to 280° C. and containing C_5 to C_9 olefins, diolefins and aromatics, said resin having an average molecular weight of about 1,000 to 5,000, said high-energy propellant solid particles being a mixture of a finely-divided fuel selected from the group consisting of lithium, aluminum, beryllium, boron, magnesium, hydrazine diborane and hydrazine monoborane, and of oxidizer particles of the group consisting of ammonium perchlorate, lithium perchlorate, sodium perchlorate, nitrocellulose, hexanitroethane and sodium nitrate.

2. A solid rocket propellant as defined in claim 1, in which the finely-divided fuel particles are powdered aluminum and the oxidizer particles are ammonium perchlorate particles.

3. A solid rocket propellant as defined in claim 1, in which hydrazine diborane particles are present as high-energy propellant solid particles.

4. Method of making a solid rocket propellant composite having good tensile strength which comprises, mixing finely-divided high-energy solid components including fuel particles from the group consisting of lithium, aluminum, beryllium, boron, hydrazine diborane and hydrazine monoborane, and oxidizer particles from the group consisting of ammonium perchlorate, lithium perchlorate, sodium perchlorate, nitrocellulose, hexanitroethane and sodium nitrate, with about 1 to 10 wt. percent based on the propellant composite of a hydrocarbon resin made by polymerizing with a Friedel-Crafts catalyst a petroleum fraction containing C_5 to C_9 olefins, diolefins and aromatics in the boiling range of 20° to 280° C., said resin having an average molecular weight of about 1,000 to 5,000 and a softening point between about 50° and 110° C., and molding the resulting mixture under superatmospheric pressure.

5. The method according to claim 4, in which the resin is dissolved in an inert solvent when it is mixed with the high-energy solid components and the solvent is removed prior to molding.

6. A method for developing thrust in a rocket from finely-divided solid propellant components of high-energy value in the combustion chamber of the rocket which comprises, combusting said components composited and held together in a mold grain containing 1 to 10 wt. percent of a hydrocarbon resin binder that gives the grain increased tensile strength, said hydrocarbon resin being made by polymerizing with a Friedel-Crafts catalyst a steam-cracked petroleum fraction boiling in the range of 20° to 280° C. and containing C_5 to C_9 olefins, diolefins and aromatics, said resin having a molecular weight of about 1,000 to 5,000, said finely-divided components including a finely-divided fuel from the group consisting of lithium, aluminum, beryllium, boron, magnesium, hydrazine diborane and hydrazine monoborane, and a compatible oxidizer from the group consisting of ammonium perchlorate, lithium perchlorate, sodium perchlorate, nitrocellulose, hexanitroethane, and sodium nitrate.

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