

[54] **SOLID PROPELLANT HAVING A FERROCENE CONTAINING POLYESTER FUEL BINDER**

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[51] Int. Cl. **C06d 5/06**

[58] Field of Search 149/19, 20, 38, 44, 19.2, 149/19.5

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

Ferrocene Polyesters that are prepared by the equation: $HO_2C(R)CO_2H + HO(R)OH \rightarrow HO_2C[(R)-CO_2(R)-O_2C]_x RCO_2H$ wherein HO-(R)-OH is a difunctional alcohol and $HO_2C(R)CO_2H$ is a difunctional acid, and (R) belongs to the group comprising alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl or alkynyl radicals which may be substituted by one or more ferrocenyl groups.

4 Claims, No Drawings

SOLID PROPELLANT HAVING A FERROCENE CONTAINING POLYESTER FUEL BINDER

This a division of application Ser. No. 730,633 now abandoned filed May 20, 1968.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Ferrocene and ferrocene derivatives have been used to give improved combustion stability and increased burn rates. One of the long recognized problems associated with the use of these compounds has been the relatively high mobility and vapor pressure of ferrocene and ferrocene derivatives. Associated with this problem is the fact that this high mobility and high vapor pressure limits the amount of ferrocene compound which can be used in a practical propellant since losses through volatility and bleeding are severe at high levels of incorporation of organometallic compounds. In some instances nonvolatile solid ferrocene derivatives are used to give decreased mobility and volatility. When the object of the additive is to obtain high burning rates, large amounts of ferrocene compounds must be used. However, large amounts of solid ferrocene or solid ferrocene derivatives are used to the detriment of practical processability. This invention solves the problems associated with volatility and bleeding out of ferrocene derivatives by incorporating the catalysts as an agent which is chemically bonded into the propellant binder. The catalytic agent is thereby prevented from being lost except by rupture of a bond by a chemical reaction.

2. Description of the Prior Art

One of the greatest problems to be overcome in this particular field of endeavor is producing either chemically or mechanically, procedures that will increase the burning rate of a composite solid propellant in a solid propellant rocket motor to increase the efficiency of the solid propellant rocket motor during operational flights. One of the procedures previously followed related to particle size of the particular oxidizer that was used in the composite solid propellant and it had been found that it was necessary to use very small particles of oxidizer in the composite solid propellant in order to achieve high burning rates.

In order to overcome the extra expense involved in producing the fine particles of oxidizer, the instant invention was developed whereby high burning rates were made available without the extra expense involved in producing oxidizer having very small particle sizes.

SUMMARY OF THE INVENTION

This invention relates, therefore, to the area of composite solid propellants and solid propellant binders in which ferrocene types compounds are used to give stable combustion and increased burning rates, and more specifically to polyester propellant binders in which organometallic moieties are included as integral parts of the binder.

One of the most important advantages which accrue from the instant invention is that in addition to the ferrocene unit which is chemically bonded into the propellant binder, other solid or liquid ferrocene compounds may be added up to levels which induce problems with processing, bleeding or volatility. In this manner much larger amounts of burning rate catalysts may be incorporated in the composite solid propellant, and

extremely high burning rates may be achieved without the problems previously encountered.

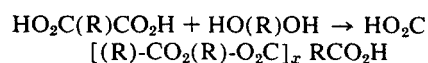
The primary object of this invention, therefore, is to provide ferrocene polyesters that will give composite solid propellants stable combustion and increased burning rates.

Another object of the invention is to provide ferrocene polyester binders in which organometallic moieties are included as integral parts of the binder.

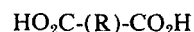
While only certain objects and advantages of the invention have been set forth, it is believed that other objects and advantages will become apparent to one skilled in the art from the following detailed description and discussion.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Liquid plasticizable, curable ferrocene containing polyesters have been prepared conveniently and in good yield. In general, the polymers are prepared from the appropriate acid and the appropriate glycol according to the reaction shown:



in which one of the comonomers is a difunctional alcohol of the general structure $\text{HO}-(\text{R})-\text{OH}$ in which (R) is an alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, or alkynyl group, and may be substituted by one or more ferrocenyl or substituted ferrocenyl groups, and in which the carbon chain may contain or may be substituted by groups containing sulfur, oxygen, halogen, nitrogen, or metallic atoms, and in which one of the comonomers is a difunctional acid of the general structure:



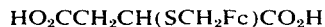
in which (R) is as described above and in which one or more comonomers contain at least one ferrocenyl or substituted ferrocenyl group as an integral part of one of the repeating units. The polyester is terminated by hydroxyl or carboxyl groups, or both, according to the conditions of the reaction. In the instance of termination by carboxylic acid groups, the polyester is cured by means of common aziridiny or epoxide-type curing agents. When the polyester is terminated by hydroxyl groups, the polyester is cured by means of common isocyanate or carboxylic acid anhydride curing agents.

The preparation of the ferrocene containing polyester embodying the invention is illustrated by the following:

EXAMPLES

A mixture of (hydroxymethyl)ferrocene (21.6 g., 0.100 mole) and mercaptosuccinic acid (30.0 g., 0.200 mole) contained in 200 ml. of water was stirred and brought to the reflux temperature, after which it was allowed to stand until it reached room temperature. The resulting solid was recovered by vacuum filtration and washed several times with water. The solid was taken up in ether and extracted several times with 5 percent aqueous sodium bicarbonate. The extractions were combined, gravity filtered, and neutralized by addition to 10 percent hydrochloric acid. The precipitate which resulted was extracted with ether. The ethereal solution was washed with water until neutral to litmus. The ether layer was dried over anhydrous magnesium

sulfate, filtered (gravity) and the solvent removed in vacuo. (Ferrocenylmethylthio)succinic acid, M.P. 177°-179°, was recovered in an amount equal to 78 percent (27.7 g) of the theoretical yield. Infrared analysis agreed with the structural assignment:



where Fc represents ferrocenyl.

The (ferrocenylmethylthio)succinic acid prepared above (11.48 g., 0.033 mole), 2-butene-1,4-diol (2.64 g., 0.030 mole), and p-toluenesulfonic acid monohydrate (0.07 g., 0.5 percent of the other constituents by weight) were placed in 80 ml. of toluene and allowed to reflux for four hours. The orange solution was filtered, while hot, through glass wool into approximately 250 ml. of n-hexane. The polymer separated to the bottom on standing, and the supernatant liquid was decanted. The polymer was taken up in acetone and poured into n-hexane after which the precipitation-decantation procedure was repeated. The polymer was taken up in acetone and the solution poured through a column containing a small amount of alumina (acid washed). Residual polymer was eluted with more acetone, the solutions combined, and the solvent removed in vacuo with heat (approximately 40°C). A clear, orange, viscous but mobile polymer was recovered in an amount equal to 76 percent (9.94 g.) of the sum of the monomers less the theoretical amount of water evolved. Infrared analysis agreed with the structural assignment:



carboxyl content was found by titration to be 0.1076 eq/100 g. for the polymer obtained by this preparation. Assuming the functionality to equal 2, the molecular weight is calculated to be 1,859. The following analysis was obtained, by ashing, for iron: found Fe, 14.7 percent; calculated Fe, 14.4 percent.

In a similar manner a mixture of 1, 5-pentanediol and ethylene glycol (75/25 by mole percent) was allowed to react with (ferrocenylmethylthio)succinic acid to afford a ferrocene containing polyester which exemplified a product prepared from a reaction in which more than one polyfunctional alcohol was used.

The resulting polyester was similar in appearance and physical properties to the previously described polymer.

It was also determined that an excellent solid propellant composition comprising the following ingredients could be provided: 2 to 90 percent of a solid oxidizer such as ammonium perchlorate, ammonium nitrate or RDX; 2 to 40 percent of a polymeric binder, as embodied in the instant invention, 0 to 50 percent of a metal-

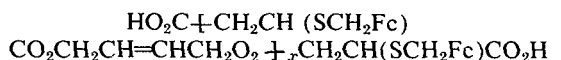
lic fuel, 0 to 25 percent of additives such as plasticizers, burning rate catalysts, cure catalysts, combustion stabilizers, and 0 to 30 percent of a non-metal containing polymeric fuel binder such as a hydrocarbon polymer.

5 It was also determined that tris-(2 methylaziridinyl)-phosphine oxide and dibutylcarbutol formal could be used in the foregoing composition to provide excellent results as a curing agent and as a plasticizer respectively. It was also determined that the solid propellant composition possessed good physical properties.

10 It is to be understood, therefore, that while the present invention has been described by means of the foregoing examples, many obvious modifications and variations will occur to those with ordinary skill in the art and it is to be further understood that such variations and modifications may be adhered to without departing from the original spirit of the invention, and the scope of the appended claims.

What is claimed is:

1. In a solid propellant composition comprising; an oxidizer selected from the group consisting of ammonium perchlorate, ammonium nitrate and RDX, a metallic fuel and a polymeric binder, the improvement comprising:
 - 25 said binder comprising a ferrocene polyester consisting essentially of the reaction product of 2-butane-1,4-diol and (ferrocenylmethylthio) succinic acid.
2. A solid Propellant composition as in claim 1, wherein the polymeric binder is



wherein x is equal to a number resulting in molecular weight of 1.859.

3. A composite solid propellant composition comprising a solid oxidizer selected from the group consisting of ammonium perchlorate, ammonium nitrate and RDX, a metallic fuel and a polymeric binder, the improvement comprising:
 - 40 said polymeric binder being a ferrocene polyester consisting essentially of the reaction product of 1,5-pentanediol and (ferrocenylmethylthio) succinic acid.
4. In a solid propellant composition comprising a solid oxidizer selected from the group consisting of ammonium perchlorate, ammonium nitrate and RDX, a metallic fuel and a polymeric binder, the improvement comprising:
 - 45 said polymeric binder being a ferrocene polyester consisting essentially of the reaction product of 1,5-pentanediol, ethylene glycol, and (ferrocenylmethylthio) succinic acid.

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