

- [54] **FERROCENE CONTAINING MONOMERS AND COPOLYMERS**
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- [58] Field of Search **260/83.5, 439 CY**

[56] **References Cited**
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[57] **ABSTRACT**

The ferrocene-containing polymerizable monomers, pentaerythritol methacrylate tris (ferrocenoate) and pentaerythritol acrylate tris (ferrocenoate), are disclosed along with the pertinent preparative procedures therefor. The specified ferrocene-containing monomers when copolymerized with butadiene serve as the propellant binder and catalyst for fast-burning composite propellants. The copolymers perform the functions of binder and catalyst in a propellant composition containing ammonium perchlorate, a plasticizer, and aluminum metal fuel.

5 Claims, No Drawings

FERROCENE CONTAINING MONOMERS AND COPOLYMERS

BACKGROUND OF THE INVENTION

Prior art compounds resulting from the selective partial esterification of pentaerythritol are known. Two derivatives of pentaerythritol which serve as the starting compounds for the preparation of the ferrocene containing monomers of this invention are pentaerythritol arsenite methacrylate and pentaerythritol arsenite acrylate.

The term polymerizable monomer is well known. The term when applied to the propellant art generally means a compound useful in propellants because it is capable of forming an elastic tough rubbery polymer by condensation or polymerization reactions in the propellant mix. The resulting rubbery polymer functions as a binder for the propellant charge. The binder provides strength for the propellant charge or grain. Many of the prior art compounds have been concerned with binder materials. The present trend has been to increase the performance of propellants by employing an energetic binder material, improved oxidizer, and burning rate catalyst.

The prior art esters of polymerizable compounds have been employed as energetic binder materials having oxidizing and plasticizing capabilities. The term energetic binder is a term to distinguish one type of binder from another type of binder known as non-energetic binder. The non-energetic binders provide binding functions while contributing little, if any, to the propellant burning processes. The propellant burning process is a complex process requiring a proper balance of fuel, oxidizer, and catalysts. The oxygen content of a number of energetic binders of the prior art enables those binders to contribute to the oxidizing capability of the propellant composition in addition to the binding capability of the propellant composition. Each active ingredient in a propellant composition contributes to one or more functions of the propellant system. Naturally, a multi-functional ingredient offers distinct advantages.

Generally, a burning rate additive has been required for use in the prior art propellant compositions to obtain increased burning rates. These additives or catalysts have included metallic oxides and organo-metallic compounds. Ferrocene and n-butyl ferrocene have been utilized as burning rate catalysts. The liquid ferrocene compounds have been effective in promoting burning rates. However, like all liquids used as additives, the characteristic disadvantages of liquid additives such as loss by evaporation, migration, etc., have caused processing problems as well as problems encountered later during long term storage of propellants.

An additive which is not subject to the disadvantages of some of the prior art compounds would be attractive for use in propellants.

The present invention has as its principal object to provide ferrocene-containing monomers which can be polymerized to form an energetic binder having a burning rate catalyst as an integral part thereof.

Another object is to provide copolymerization products of ferrocene-containing monomers and butadiene which serves as energetic binder and burning rate catalyst for propellant compositions.

A further object of this invention is to provide a propellant composition having a combination energetic

binder and catalyst which does not evaporate during propellant processing or migrate in the finished propellant.

SUMMARY OF THE INVENTION

The ferrocene-containing monomers, pentaerythritol methacrylate tris (ferrocenoate) and pentaerythritol acrylate tris (ferrocenoate) are produced from pentaerythritol arsenite methacrylate and pentaerythritol arsenite acrylate respectively as the starting compounds. The monomers become constituents of copolymers of butadiene when polymerization reaction is initiated by a suitable initiator. The copolymers of this invention are useful as binders for solid propellants which also contain an oxidizer, metal fuel, and plasticizer. The binders also function as a burning rate catalyst since the catalyst is an integral part thereof. The catalyst being an integral part of the cured binder does not migrate during propellant storage. The catalyst is evenly and widely dispersed as an integral part of the binder; therefore, this arrangement is conducive to uniform burning rate control and stability to burning of the propellant composition.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The starting compound, pentaerythritol arsenite methacrylate, forms one of the monomers of this invention and may be produced as follows.

To a clear solution of 10.4 grams (0.050 mole) of pentaerythritol arsenite in 20 milliliters of acetonitrile and 8 milliliters of triethylamine is added drop wise a mixture of 5.5g. (0.052 mole) of methacryloyl chloride and 5 ml. of acetonitrile. The addition requires about 15 minutes while the temperature is maintained at about 35°C to about 40°C by external cooling. The mixture is stirred at 50°C for 2 hours, then the solvent is removed at reduced pressure, and the residue is dried at ambient temperature and 1 millimeter of pressure for 30 minutes. The residue is extracted with three 100 ml. portions of hot ligroin (each containing 5 mg. of hydroquinone). The extracts are concentrated and chilled and the product removed by filtration. The solid obtained is recrystallized from ligroin to give 5.40 grams of the monomer, pentaerythritol arsenite methacrylate, m.p. 83°C to 84.5°C.

Another starting compound pentaerythritol arsenite acrylate, forms another monomer and may be produced as follows.

To a mixture of 10.4g. (0.050 mole) of pentaerythritol arsenite and 10 ml. of acetonitrile is added 4.5 ml. (0.065 mole) of acrylic acid followed by 24 ml. (0.175 mole) of triethylamine. When the exotherm from the addition of the amine (the reaction temperature should not be allowed to exceed 20°C) is subsided, 7.7 ml. (0.060 mole) of benzene-sulfonyl chloride in 10 ml. of acetonitrile is added over a 15 minute period. The reaction mixture is cooled to keep the temperature below 30°C during the addition; after the benzenesulfonyl chloride addition, the mixture is stirred at 30°C for 1 hour. The solvent is then removed at reduced pressure and the residue dried at ambient temperature and 1 millimeter of pressure for 30 minutes. The residue is extracted three times with 200 ml. of hot ligroin containing 0.01g of hydroquinone. The residue is taken up in methylene chloride and again stripped to dryness. Recrystallization from ligroin yields the monomer,

pentaerythritol arsenite acrylate, 7.4 g. m.p. 80°C to 82°C.

Pentaerythritol methacrylate tris (ferrocenoate) and pentaerythritol acrylate tris (ferrocenoate) are monomers which are prepared as set forth hereinbelow under Example I and II. The specified monomers when copolymerized with butadiene form binders that provide in addition to the binder function the function of catalysis for the propellant system wherein used. Example III and Example IV are illustrative of the procedures for preparation of the copolymers of this invention. Table I sets forth burning rates of uncured composite propellants using the hydroxy-terminated copolymer of butadiene and pentaerythritol methacrylate tris (ferrocenoate) as compared with a propellant using unmodified hydroxy-terminated polybutadiene, and a propellant using n-butyl ferrocene, a standard burning-rate promoter. Similarly, the copolymer of pentaerythritol acrylate tris (ferrocenoate) and butadiene may be used as the binder and catalyst for a propellant composition.

EXAMPLE I

Preparation of Pentaerythritol Methacrylate Tris (ferrocenoate)

A 2.20 g. (8 mole) sample of pentaerythritol arsenite methacrylate and 20 mg. of dicyanobenzoquinone is stirred with 25 ml of acetone and 6 ml of water for 30 minutes at 40°C. The solution is filtered, and the filtrate is stripped to dryness. The residue, in methylene chloride, is dried over calcium sulfate. The solution is again stripped to dryness, and the residue taken up in 8 ml methylene chloride and 8 ml of chlorobenzene. This solution is added to 8.44 g. of ferrocenoyl chloride in 18 ml of chlorobenzene in a flask maintained at 200-mm pressure. When addition is complete, the pressure is reduced to 150 mm and the temperature is maintained at 50°C for 1 hour. The chlorobenzene is removed in vacuo and the residue is partitioned between methylene chloride and water. The organic residue is chromatographed on a silica gel column packed in pentane-methylene chloride (2:1 and 1:1), and methylene chloride gives a center cut of 1.69 g. This portion is re-crystallized from methanol to give pentaerythritol methacrylate tris (ferrocenoate), 1.14g, m.p. 109-112°C.

Analysis

Calculated for $C_{42}H_{40}Fe_3O_8$: C, 60.0; H, 4.80; Fe, 19.94.
Found: C, 59.7; H, 4.80; Fe, 20.9

EXAMPLE II

Preparation of Pentaerythritol Acrylate tris (ferrocenoate)

The procedure outlined in Example I above is followed using 1.71 g of pentaerythritol monoacrylate

(prepared by hydrolysis of pentaerythritol arsenite acrylate) and 10 g. of ferrocenoyl chloride. The organic residue obtained upon evaporation of the organic solvents is re-crystallized from methanol. The yield is pentaerythritol acrylate tris (ferrocenoate), 1.05 g, m.p. 107-109°C.

Analysis

Calculated for $C_{41}H_{38}Fe_3O_8$: C, 59.60; H, 4.64; Fe, 20.3.
Found: C, 59.1; H, 4.59; Fe, 19.7.

EXAMPLE III

Copolymerization With Butadiene

Introduce to a glass high-pressure reactor (Aerosol tube): 30 ml. of toluene, 2.112g (0.0084 mole) azo-bis-(2-methyl-5-hydroxy-valeronitrile) as initiator, and 2.1g (0.0025 mole) pentaerythritol methacrylate tris (ferrocenoate). The reactor is attached to a vacuum line and deaerated by three alternate freeze-thaw cycles. Butadiene (10.8g., 0.2 mole) is condensed into the reactor, and the reactor transferred to an oil bath at 66-67°C. Heating is continued for a period of 72 hours. On cooling the solvent is removed by evaporation and the copolymer reprecipitated by dissolving in ether followed by the addition of methanol. After decanting the solvents, the copolymer is stripped of excess solvents on a rotatory evaporator and finally dried at 70-75°C. under reduced pressure (1 mm) for a period of 24 hours. The yield of liquid copolymer is 7.1 g (55%). The copolymer is characterized by molecular weight (3,500), OH end groups (1.21 wt%) and elemental analysis (Fe, Found: 3.9).

EXAMPLE IV

In a similar reaction to that set forth in Example III, 5.4 g. (0.1) butadiene is copolymerized with 2.1g (0.0025 mole) of pentaerythritol methacrylate tris (ferrocenoate) in toluene with 0.756 g. (0.003 mole) azo-bis-(2-methyl-5-hydroxy-valeronitrile) as initiator to give 4.2 g. (56%) of the copolymer analyzing as follows: molecular weight (4,700), OH end groups (0.8 weight%) and elemental analysis (Fe, Found 6.9%).

As noted in Examples III and IV the mole ratio of butadiene to monomer is from about 40 to 1 to about 80 to 1 for the monomer selected. The mole ratio in Examples III and IV is also satisfactory when the monomer pentaerythritol acrylate tris (ferrocenoate) is selected for copolymer preparation.

Burning Rate Data

The hydroxy-terminated copolymer of butadiene and pentaerythritol methacrylate tris (ferrocenoate) containing 3.9% Fe, (prepolymer A of Table I), provides a significant increase in propellant burning rate: Table I below summarizes the data as compared with the standards set forth therein.

Similarly, the hydroxy-terminated copolymer of butadiene and pentaerythritol acrylate tris (ferrocenoate) may be used in place of the prepolymer, butadiene and pentaerythritol methacrylate tris (ferrocenoate).

Table I

Burning Rates of Uncured Composite Propellants						
Prepolymer %	Plasticizer %	NH ₂ ClO ₄ %	Al %	Additive %	R _b at 750 psi	R _b at 1500 psi
HTPB* 10	Isodecyl Pelargonate	70	10	—	0.54	0.84
A	Isodecyl Pelargonate	70	10	—	0.71	0.97
HTPB* 8	Isodecyl Pelargonate	70	10	NBF** 2	0.71	0.97

* Unmodified hydroxy-terminated polybutadiene.

** n-butyl ferrocene, a standard burning-rate promoter.

Isodecyl pelargonate is available under the trademark, Emolein from Emery Industries, Inc. Other suitable plasticizers include diisooctyl azelate, di-2-ethylhexyl azelate, and dipropylene glycol dipelargonate.

The plasticizers noted above may be used with the copolymers of this invention in amounts from about 5 to about 25 weight percent of the propellant composition. The ammonium perchlorate may vary from about 50 to about 70 weight percent of the propellant composition. The copolymers of this invention may be used in propellant compositions in amounts from about 5 to about 30 weight percent. Aluminum metal from about 5 to about 20 weight percent may be used in the propellant composition containing the copolymers of this invention.

The copolymers of this invention may be substituted for polybutadiene and the burning rate catalyst employed in a propellant composition since the copolymers contain a catalyst as an integral part thereof. The copolymers of this invention are particularly attractive as a source of catalysis for the propellant composition in order to avoid the problems associated with the use of liquid catalysts (e.g. problems, such as, loss by evaporation or migration within the propellant during storage).

We claim:

1. A polymerizable monomer selected from pentaerythritol methacrylate tris (ferrocenoate) and pentaerythritol acrylate tris (ferrocenoate) reacted with bu-

tadiene to form a copolymer.

2. The copolymer of claim 1 wherein said butadiene and said selected monomer are reacted in the presence of a suitable initiator contained in a suitable organic solvent for a predetermined period of time and at a predetermined temperature; said butadiene and said selected monomer being present in a mole ratio of butadiene to monomer from about 40 to 1 to about 80 to 1.

3. The copolymer of claim 2 wherein said selected monomer is pentaerythritol acrylate tris (ferrocenoate); said suitable solvent is toluene; said predetermined period of time is about 72 hours; said predetermined temperature is from about 66°C to about 67°C; and said suitable initiator is azo-bis-(2-methyl-5-hydroxy-valeronitrile).

4. The copolymer of claim 2 wherein said selected monomer is pentaerythritol methacrylate tris (ferrocenoate); said suitable solvent is toluene; said predetermined period of time is about 72 hours; said predetermined temperature is from about 66°C to about 67°C; and said suitable initiator is azo-bis-(2-methyl-5-hydroxyvaleronitrile).

5. The copolymer of claim 4 characterized by a molecular weight in the range from about 3500 to about 4700, OH end groups from about 0.8 to 1.2 weight percent, and Fe content from about 3.9 to about 6.9 weight percent.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,857,870 Dated 12/31/74

Inventor(s) Travis E. Stevens et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the Cover Sheet, item [73] should read
Assignee:

United States of America as respresented
by the Secretary of the Army.

Signed and sealed this 3rd day of June 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,857,870 Dated 12/31/74

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