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(54) **Hydrocarbon fuels containing antimisting agents.**

(57) Hydrocarbon fuel compositions having reduced tendency to form an explosive mist under shock are prepared by combining a high molecular weight copolymer of butene-1 and at least, one other alpha-monoolefin with the hydrocarbon fuel.

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BACKGROUND OF THE INVENTION

This invention relates to hydrocarbon fuels and more particularly to hydrocarbon fuels having a reduced tendency to form an explosive mist when subjected to shock.

When hydrocarbon fuels are subjected to severe shock, there is a tendency for the fuel to atomize and form a mist which upon contact with a spark or hot engine part can ignite and form a fire ball. The problem is particularly acute in crashes of aircraft in which the fuel spills out of the plane upon impact. The impact in combination with the sudden rush of air causes the fuel to rapidly atomize and form a large highly explosive mist. Fires caused from ignition of mist formed when planes crash often envelope the aircraft and cause the death or serious injury of many passengers who would survive the crash in the absence of the fire. For many years, the Federal Aviation Administration has tested antimisting additives which when added to jet fuels would reduce or eliminate the hazard of flash fires in aircraft crashes. Early research efforts were based on the use of thixotropic agents which, when incorporated into hydrocarbon fuels, caused the fuel to gel upon sudden impact. These compositions proved unsatisfactory, however, because of the weight and pumping problems associated with the use of these compositions.

PRIOR ART

High molecular weight organic polymers have for sometime been investigated for use as antimisting agents for hydrocarbon fuels. U.S. Patent 3,998,605, issued to

Osmond et al, discloses the use of a copolymer of ethylene and a higher olefin as an additive for gas turbine aviation fuels to reduce the tendency of the fuel to form mist particles under shock conditions. U.S. Patent 3,925,032, issued to Osmond et al, discloses the use of alkylstyrene homopolymers and copolymers as additives for aircraft fuels to reduce the tendency of the fuel to particulate dissemination when subjected to shock. U.S. Patent 3,996,02 issued to Osmond et al, discloses the use of copolymers of ethylenically unsaturated hydrocarbons such as isobutylene, butadiene, isoprene and mixtures of ethylene and propylene. This patent also discloses that higher olefins such as pentene, hexene and higher homologs may be included in the polymer but states that these olefins tend to reduce the chain length to weight ratio. U.S. Patent 4,356,003, issued to Brooks et al, discloses the use of terpolymers of tertiary butylstyrene, methacrylic acid and a third monomer selected from acrylic and methacrylic esters of aliphatic monohydric alcohols, acrylonitrile, vinyl acetate, styrene and vinyl toluene. European Patent Application publication number 0,019,390, issued to Brooks et al, also discloses a terpolymer of tertiary butylstyrene, acrylic and methacrylic esters of aliphatic monohydric alcohols and methacrylic acid as a polymeric additive for aviation fuels. U.S. Patent 4,289,679, issued to Mack, discloses the preparation of homopolymers and copolymers of alpha-monoolefins. This patent states that these polymers are useful as antimist agents for fuels. These patents show the considerable effort that has been put into research to find additives for fuels which will reduce or eliminate the tendency of the fuel to form a mist when subjected to a shock, and yet will not adversely effect the other desirable properties of a fuel, such as low temperature pumpability. Although some of the above described polymeric materials are effective in reducing the misting tendency of fuels, none of them is completely satisfactory from an overall standpoint. There is a continuing need for improved fuel antimisting agents.

SUMMARY OF THE INVENTION

The present invention discloses high molecular weight polymeric fuel antimist additives which have superior antimisting properties. Accordingly, it is an object of the invention to present novel antimisting agents for hydrocarbon fuels. It is another object of the invention to present high molecular weight polymeric materials which effectively reduce the tendency of hydrocarbon fuels to form an explosive mist upon impact. It is another object of the invention to present a method of reducing the tendency of hydrocarbon fuels to form explosive mists upon impact. It is another object of the invention to present aircraft fuels which resist the tendency to form explosive mists when subjected to shock. These and other objects of the invention are supported in the following description and examples.

The benefits of the invention are realized by incorporating into a hydrocarbon fuel small amounts of a high molecular weight copolymer of butene-1 and at least one other alpha-monoolefin having 5 or more carbon atoms. In a preferred embodiment of the invention the molecular weight of the copolymer is at least 500,000 and most preferrably is in the range of about 1 to 20 million. It is also preferred that the concentration of the copolymer in the hydrocarbon fuel is in the range of about 0.001 to 5 percent and more preferably about 0.01 to 2 percent based on the total weight of hydrocarbon fuel composition. Preferred copolymers are those of butene-1 and at least one alpha-monoolefin having 5 to 20 carbon atoms and most preferrably 6 to 14 carbon atoms.

## DETAILED DESCRIPTION OF THE INVENTION

The copolymers of the invention are comprised of butene-1 and at least one other alpha-monoolefin having 5 or more carbon atoms. Preferred copolymers are those of butene-1 and at least one other alpha-monoolefin having 5 to 20 carbon atoms. Although alpha-monoolefins having more than about 20 carbon atoms can be used in the invention, those having 20 or fewer carbon atoms are preferred due to their commercial availability.

The polymeric compositions of the invention are prepared from butene-1 and one or more higher alpha-monoolefins. When a two alpha-monoolefin component system is employed the butene-1 and the other alpha-monoolefin component are usually present in the reaction mixture in an amount sufficient to produce a copolymer containing at least 10 mole percent of each component. In the preferred embodiments of the two alpha-monoolefin component system each component is present in an amount sufficient to produce copolymers containing 25 or more mole percent of each component. In three or more alpha-monoolefin component systems it is preferred that the maximum content of any one monomer is 90 mole percent and most preferably 75 mole percent, based on the total number of moles of butene-1 and the other alpha-monoolefin monomers present in the reaction mixture.

Typical copolymers which are usable in the invention are those prepared from butene-1 and one or more of hexene-1, octene-1, decene-1, dodecene-1, hexadecene-1, eicosene-1, etc. Preferred copolymers are those prepared from butene-1 and one or more of hexene-1, octene-1, decene-1, dodecene-1, tetradecene-1, etc. Examples of preferred copolymers include butene-1-hexene-1 copolymer, butene-1-octene-1 copolymer, butene-1-decene-1 copolymer, butene-1-dodecene-1 copolymer and butene-1-tetradecene copolymer. Preferred terpolymers include butene-1-hexene-1-decene-1 terpolymer, butene-1-octene-1-dodecene-1 terpolymer, etc.

The copolymers of the invention desirably have a weight average molecular weight of at least 500,000 and are generally in the range of 500,000 to 20 million. There is no upper molecular weight limit and polymers having any weight average molecular weight above about 500,000 are usable. At the lower end of the scale polymers having weight average molecular weight significantly below about 500,000 are not as desirable as those having weight average molecular weight of at least 500,000. In a preferred embodiment the weight average molecular weight is in the range of about 1 to 20 million.

The method of polymerization of the monomers is not a part of the invention. In general, any of the several well known methods for polymerizing alpha-monoolefins can be employed. A particularly suitable method is the

Ziegler process using catalyst systems comprising combinations of a compound of a metal of Groups IV-B, V-B, VI-B or VIII of the Periodic Chart of the Elements found on pages 392-393 of the Handbook of Chemistry and Physics, 37th Edition with an organometal compound of a rare earth or metal from Groups I-A, II-A, or III-A of the Periodic Chart of the Elements. Particularly suitable catalyst systems are those comprising titanium halides and organoaluminium compounds. A typical polymerization procedure is to contact the monomeric mixture with the catalyst in a suitable inert hydrocarbon solvent for the monomers and the catalyst in a closed reaction vessel at reduced temperatures and autogenous pressure and in a nitrogen atmosphere. Further details of the Ziegler process are set forth in U.S. Patent 3,692,676, which is incorporated herein by reference.

GB-A-2074175, incorporated herein by reference, describes copolymers which are suitable for use in this invention.

The hydrocarbon fuels in which the copolymer of the invention may be used include kerosene, jet fuel, naphtha, gasoline, etc. The copolymers are particularly effective in jet aviation fuels such as grade JP-8, specified in U.S. Military Specification MIL-T-83133, grade JP-5 (flash point 140°F minimum) as specified in U.S. Military Specification MIL-T-5624G, grades Jet A and Jet A-1 (flash point 110°F minimum) as specified in U.S. Military Specification MIL-T-D1655/66T, etc.

The copolymer is added to the hydrocarbon fuel at a concentration which is effective to eliminate or substantially reduce the tendency of the hydrocarbon fuel to form a highly explosive mist upon being subjected to shock. In general, this is accomplished by incorporating the copolymer into the hydrocarbon fuel at a concentration of about .001 to 5 percent based on the total weight of hydrocarbon fuel composition. The preferred concentration of copolymer in the hydrocarbon fuel composition is in the range of about .01 to 2 percent based on the total weight of the hydrocarbon fuel composition. The concentration of copolymer in the hydrocarbon fuel which produces the optimum result will vary depending on the particular co-monomers from which the copolymer is prepared, the molecular weight of the copolymer and the hydrocarbon fuel being treated. Other fuel additives can be used in combination with the copolymers in the invention. For example, corrosion inhibitors, antioxidants, etc. can be added to the hydrocarbon fuel formulation, as desired.

In preparing the stabilized hydrocarbon fuel compositions of the invention, the copolymer in the desired concentration is dissolved in the hydrocarbon fuel. This can be accomplished by adding the copolymer directly to the fuel or by adding a solution of the copolymer and a compatible hydrocarbon solvent to the hydrocarbon fuel. Upon addition of the copolymer to the hydrocarbon fuel, the mixture is agitated sufficiently to completely dissolve the copolymer in the hydrocarbon fuel. This can be easily accomplished, as the copolymers are readily soluble in hydrocarbon fuels.

The following examples illustrate specific embodiments of the invention. Unless otherwise indicated parts and percentages are on a weight basis.

The following examples were carried out using the full scale wing spillage test practised by the Federal Aviation Administration at its Atlantic City, New Jersey technical center. In the test a stream of air is directed across the leading edge of an aircraft wing section at a predetermined velocity. A fuel formulation to be tested is then forced through an orifice in the leading edge of the wing into the counterflowing air stream. A propane torch is located aft of and below the fuel release point. This torch, which in still air produces a flame 5 feet long, 8 inches in diameter and 1100°F in temperature serves as the ignition source. Further details of the test can be obtained from Report No. FAA-CT-81-181, page 2-1, available through the National Technical Information Service, Springfield, Virginia.

EXAMPLE I (Comparative)

Untreated Jet A fuel was tested according to the above procedure at a fuel spillage rate of 20 gallons per second and at a relative air velocity of 130 knots. A huge fireball formed and propagated against the flow of air to the most forward point in the fuel stream.

EXAMPLE II

The test of Example I was repeated using Jet A fuel containing 0.1 weight percent of a butene-1-dodecene-1 copolymer having an inherent viscosity of 13.0 dl/g. The modified fuel did form an ignitable mist. Small fireballs formed but self-extinguished before contacting the ground. There was little or no tendency of the ignited fuel to propagate toward the ignition source.

EXAMPLE III

The procedure of Example II was repeated except that the air speed was 120 knots. The fuel had no propensity to ignite.

CLAIMS:

1. A hydrocarbon fuel composition having a reduced tendency to form an explosive mist when subjected to shock comprising a hydrocarbon fuel and about 0.001 to 5% based total weight of said composition of a high molecular weight copolymer of butene-1 and a second component comprising at least one alpha-monoolefin having 5 or more carbon atoms.

2. A method of reducing the tendency of hydrocarbon fuel compositions to form an explosive mixture upon being subjected to shock comprising incorporating into said composition about 0.001 to 5% based on the total weight of said composition of a copolymer of butene-1 and a second component comprising at least one other alpha-monoolefin having at least 5 carbon atoms.

3. The composition of claim 1 or the method of claim 2 wherein said second component is at least one alpha-monoolefin having 5 to 20 carbon atoms, and said copolymer has a weight average molecular weight of at least 500,000.

4. The composition or method as claimed in any one of claims 1 to 3, wherein said hydrocarbon fuel comprises substantially kerosene, jet fuel, naphtha or gasoline.

5. The composition or method of any one of claims 1 to 4, wherein the concentration of said copolymer in the composition is about .01 to 2% based on the weight of the composition.

6. The composition or method of any one of claims 1 to 5, wherein said second component is at least one alpha-monoolefin having 6 to 14 carbon atoms.

7. The composition or method of claim 6, wherein said copolymer has a weight average molecular weight of about 1 to 20 million.

8. The composition or method of claim 6 or claim 7, wherein said second component is an alpha-monoolefin selected from hexene-1, octene-1, decene-1, dodecene-1, tetradecene-1, and mixtures of these.

European Patent Office

# EUROPEAN SEARCH REPORT

0177649

Application number

EP 84 30 6890

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
|---|---|---|---|
| | | | C 10 L 1/16 |
| D,X | GB-A-2 074 175 (ATLANTIC RICHFIELD)<br>* Claims 1,5,7-9,12-18 *<br>--- | 1-8 | |
| D,A | US-A-3 996 023 (D.W.J.OSMOND)<br>* Claims 1,2 *<br>----- | 1,5 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.4) |
| | | | C 10 L |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 06-06-1985 | ROTSAERT L.D.C. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document