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Biasotti et al.

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[54] **MOTOR FUEL ADDITIVE**

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[58] **Field of Search** ..... 44/66, 71, DIG. 1

[56] **References Cited**

UNITED STATES PATENTS

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2,902,353	9/1959	Becker et al.	44/DIG. 1
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[57] **ABSTRACT**

Diester-amide fuel additive prepared by esterifying a mole of trimer acid with two moles of an aliphatic alcohol having from 6 to 16 carbon atoms and amidating the intermediate diester reaction product with a mole of a dialkanolamine to produce a diester-amide, and a motor fuel composition containing same.

5 Claims, No Drawings

MOTOR FUEL ADDITIVE

BACKGROUND OF THE INVENTION

1. Field of the Invention

Modern internal combustion engine design is undergoing important changes to meet certain standards concerning engine and exhaust gas emissions. A major change in engine design presently being adopted is the feeding of blow-by gases from the crankcase zone of the engine into the intake air supply to the carburetor rather than venting these gases to the atmosphere as in the past. These blow-by gases contain substantial amounts of deposit-forming substances and it has been observed that some of the substances in the blow-by gases form deposits in and around the throttle plate area of the carburetor. The deposits restrict the flow of air through the carburetor at idle and low speeds so that an overrich fuel mixture results. This condition produces rough idling, engine stalling and also results in excessive hydrocarbon exhaust emissions to the atmosphere.

Modern motor fuel compositions must also possess adequate corrosion inhibiting properties. These fuel compositions are transported over long distances and stored for considerable lengths of time in steel and metal containers and it is essential that the fuel composition possess a high level of rust inhibition.

2. Description of the Prior Art

U.S. Pat. No. 3,574,574 discloses a motor fuel composition which contains a polyester of a polymerized carboxylic acid to reduce intake valve and port deposit in a gasoline engine.

U.S Pat. No. 3,561,936 discloses an anti-wear fuel oil composition containig trimer acid in a concentration of 100 to 200 lbs. per thousand barrels of fuel.

SUMMARY OF THE INVENTION

The additive of the invention, which is effective in gasoline as a carburetor detergent and as a rust inhibitor, comprises a diester-amide prepared by esterifying a mole of trimer acid produced by the polymerization of an unsaturated aliphatic monocarboxylic acid with two moles of an aliphatic alcohol to produce an intermediate diester reaction product and amidating a mole of said diester reaction product with a mole of a dialkanolamine to produce the diester amide.

The motor fuel composition of the invention comprises a mixture of hydrocarbons in the gasoline boiling range containing a minor amount of the diester-amide additive effective to provide carburetor detergency and rust inhibiting properties in the fuel composition.

SPECIFIC EMBODIMENTS OF THE INVENTION

The diester-amide fuel additive is prepared by esterifying a mole of trimer acid, which is produced by the polymerization of an unsaturated aliphatic monocarboxylic acid having between 16 and 22 carbon atoms per molecule with two moles of an aliphatic alcohol having from about 6 to 16 carbon atoms to produce an intermediate diester reaction product and amidating a mole of the intermediate diester reaction product with a mole of a dialkanolamine having the formula:

$HN\text{-}(R\text{-}OH)_2$

in which R is an alkylene radical having from 2 to 4 carbon atoms to produce a diester-amide.

The trimer acid component employed in preparing the additive of the invention is a fatty material produced by subjecting unsaturated fatty acids having between 16 and 22 carbon atoms per molecule, and preferably from 16 to 18 carbon atoms, to condensation by moderate steam pressures of from 80 to 300 psig at temperatures from 260° to 360°C. for a period of from about 3 to 8 hours. Processes for forming these acids are set forth in such patents as U.S. Pat. No. 2,632,695 and the disclosure in this patent is incorporated herein. Another method for preparing trimer acid material broadly comprises heating a short chain aliphatic alcohol ester of a diethylenic fatty acid at about 300°C. for several hours in an inert atmosphere. The resulting polymerized esters containing trimer acid material are then separated by distillation and hydrolyzed with hydrochloric acid or its equivalent. Fatty oils have also been heat polymerized and thereafter hydrolyzed to produce the polymer acid. The trimer acid is readily separated by distillation or by a solvent extraction process from the monomeric, dimeric and higher polymeric materials usually coproduced in the foregoing methods. The trimer acids used in the present invention although preferably condensation products of three of the same molecules which are di- or polyethylenic are also products of the combination of a monoethylenic compound and a polyethylenic compound for instance linoleic acid and oleic acid trimerized to become the trimer of linoleic and oleic acids. It is essential to have at least one polyethylenic compound present in order to form the trimer acid.

Specific fatty acids useful for preparing trimer acid from the class of ethylenic carboxylic acids having from 16 to 22 carbon atoms include palmitoleic, oleic, linoleic and erucic acid. The preferred acid is linoleic acid on the basis of availability from which is produced the preferred trimer of linoleic acid. A trimer acid is produced commercially by polymerization of unsaturated C_{18} fatty acids and consists of about 90 percent trimer acid, a 54 carbon tribasic acid with a molecular weight of 850.

The aliphatic alcohol which is reacted with the trimer acid is represented by the formula: ROH in which R represents a saturated aliphatic hydrocarbon radical having from 6 to 16 carbon atoms. Representative alcohols within this class include decyl alcohol, isodecyl alcohol, octyl alcohol, tetradecyl alcohol and cetyl alcohol.

The preferred alcohol for reacting with the trimer acid are the saturated aliphatic alcohols having from 8 to 12 carbon atoms with the particularly preferred alcohol being isodecyl alcohol.

The dialkanolamine reactant which is reacted with the partially esterified trimer acid is represented by the formula: $HN\text{-}(R\text{-}OH)_2$ in which R represents an alkylene radical having from 2 to 4 carbon atoms. Dialkanolamines included within this class are diethanolamine, dipropanolamine, diisopropanolamine and the dibutanolamines with diethanolamine being particularly preferred.

In preparing the diester-amide of the invention, the first step in the process is to react the trimer acid with the aliphatic alcohol. Since trimer acid has three carboxylic groups and it is desired to esterify two of these carboxylic groups a mole of trimer acid is reacted with two moles of a prescribed aliphatic alcohol under esterification conditions to produce an intermediate diester reaction product. Generally, this reaction will be conducted in the presence of a hydrocarbon or inert sol-

vent, such as xylene. The mixture is azeotrope distilled to a pot temperature of about 200°C. and the reaction continued at this temperature until the water of esterification has been collected.

A prescribed dialkanolamine is now added to the reaction mixture in the proportion of one mole of the intermediate diester reaction product to one mole of the dialkanolamine. This mixture is then reacted at a temperature ranging from about 150° to 200°C. until the reaction has been completed. The reaction product is then stripped of solvent by distillation.

The following example illustrates the preparation of a specific diester-amide additive according to this invention.

EXAMPLE I

1037 grams (1.2 moles) of commercial "Trimer Acid" produced by the polymerization of linoleic acid and consisting of about 80 percent of C_{54} tribasic acid having a molecular weight of about 850 and about 20 percent of dimer acid i.e. C_{36} dibasic acid having a molecular weight of about 565 and having an Acid Value of 183–191 and a saponification No. of 192–200 was combined with 382 grams (2.4 moles) of isodecyl alcohol in 600 ml. of xylene and the mixture azeotrope distilled to a pot temperature of 200°C. Reaction was continued at this temperature for 7 hours with the water of esterification being collected. Sufficient xylene was then added to the reaction mixture to cause reflux at a temperature of 180°C. 126 grams (1.2 moles) of diethanolamine was added and the reaction continued for five hours. Upon completion, the reaction product was stripped of solvent by distillation. The diester-amide product analyzed as follows:

Analysis	Found	Calc.
% N	0.87	1.21
OH No.	59	97
Sap. No.	145	97
TBN	9.6	0
TAN	1.6	0

The base fuel employed for preparing the motor fuel composition of the invention comprises a mixture of hydrocarbons boiling in the gasoline boiling range. This base fuel may consist of straight chain or branched chain paraffins, cycloparaffins, olefins and aromatic hydrocarbons or any mixture of these. The base fuel can be derived from straight run naphtha, polymer gasoline, natural gasoline or from catalytically cracked or thermally cracked hydrocarbons and catalytically reformed stocks. The composition or hydrocarbon components of the base fuel is not critical nor does the octane level of the base fuel have any material effect on the invention. In general, the base fuel will boil in a range from about 80°F. to about 450°F.

The fuel composition can contain any of the additives normally employed in gasoline. Thus, the fuel composition can contain an anti-knock compound such as a tetra-alkyl lead compound, including tetraethylead, tetramethylead, tetrabutylead and mixtures thereof. The fuel composition can also contain anti-icing additives, dyes, upper cylinder lubricating oils and the like.

The diester-amide additive of the invention was tested for its effectiveness as a detergent in gasoline in the Chevrolet Carburetor Detergency Test. In this test, a gasoline fuel composition containing the additive is tested for its ability to remove preformed deposits from the throttle plate area in a carburetor. This test is run on a Chevrolet V-8 engine mounted on a test stand using a modified four-barrel carburetor. The two secondary barrels on the carburetor are sealed and the feed to each of the primary barrels arranged so that the detergent additive fuel can run in one barrel and the reference fuel run in the other. The primary carburetor barrel were also modified to contain removable aluminum inserts in the throttle plate area so that the deposits formed on the inserts could be conveniently weighted.

The engine is run for a period of time usually 24 or 48 hours using the base fuel as the feed to both barrels with the engine blow-by circulated to the air inlet of the carburetor to cause a deposits build-up. The weight of the deposits on both sleeves is determined and recorded. The engine is then cycled for 24 additional hours with the reference fuel being fed to one barrel and the additive fuel to the other. During this cycle, engine blow-by is circulated to the air inlet of the carburetor. The inserts are then removed from the carburetor and weighed to determine the difference between the performances of the additive-containing fuel of the invention and the reference fuel for removing preformed deposits. After the aluminum inserts have been cleaned, they are replaced in the carburetor and the process repeated with the fuel feeds inlet to the carburetor reversed in order to minimize differences in fuel distribution and carburetor construction. The results obtained in the fuel runs are averaged and the effectiveness of the reference fuel and of the additive fuel for removing deposits expressed in percent.

The carburetor detergency test results obtained from the base fuel and the fuel composition containing the diester-amide prepared in Example I are set forth in Table I below:

TABLE I

CHEVROLET CARBURETOR DETERGENCY TEST DEPOSIT REMOVAL

FUEL COMPOSITION	Deposit Build-up mg.*	Deposit Removed, mg.	Percent Effective
1. Base Fuel	16.8	−1.7	−10
2. Base Fuel + 25 PTB Diester Amide	17.0	9.3	55
3. Base Fuel + 30 PTB Diester Amide	19.0	11.4	60

*Built up with base fuel.
PTB = pounds of additive per 1000 barrels of fuel

The fuel composition containing the diester-amide additive of the invention was outstanding as a carburetor detergent for removing preformed deposits from the throttle plate area of the carburetor.

The rust inhibiting property of the additive of the invention was determined in a fuel composition containing the diester-amide of the invention tested in the Colonial Pipeline Rust Test. This test is a modification of ASTM Rust Test D–665–60 procedure A. In the Colonial Pipeline Test, a steel spindle is polished with non-waterproof emery cloth. The spindle is immersed in a mixture containing 300 cc of fuel and 30 cc of distilled water and rotated for 3.5 hours while the mixture is maintained at 100°F. The spindle is then rated visually for the amount of rust formation. A passing result is an

average of less than 5 percent rust. The results of this test are set forth in Table II below.

TABLE II

COLONIAL PIPELINE RUST TEST	
Fuel Composition	Per Cent Rust
1. Base Fuel	90, 100
2. Base Fuel + 20 PTB Diester Amide	Less than 0.1 to 1.0
3. Base Fuel + 25 PTB Diester Amide	Less than 0.1 to 1.0
4. Base Fuel + PTB Diester Amide	Less than 0.1

While the base fuel permitted 90–100 percent rusting under the test conditions, fuel compositions containing the additive of this invention were surprisingly effective in their rust inhibiting property with test results almost entirely free of rust.

We claim:

1. A motor fuel composition comprising a major amount of a mixture of hydrocarbons in the gasoline boiling range containing a minor detergent and rust inhibiting amount of a diester-amide fuel additive prepared by esterifying a mole of trimer acid produced by the polymerization of an unsaturated aliphatic monocarboxylic acid having between 16 and 22 carbon atoms per molecule with 2 moles of an aliphatic monohydric alcohol having from about 6 to 16 carbon atoms to produce an intermediate diester reaction product and amidating a mole of said intermediate diester reaction product with a mole of dialkanolamine having the formula $HN-(R-OH)_2$ in which R is an alkylene radical having from 2 to 4 carbon atoms to produce said diester-amide.

2. A motor fuel composition according to claim **1** in which said unsaturated aliphatic monocarboxylic acid is linoleic acid.

3. A motor fuel composition according to claim **1** in which said aliphatic alcohol has from about 8 to 12 carbon atoms.

4. A motor fuel composition according to claim **1** in which said aliphatic alcohol has from about 8 to 12 carbon atoms and said dialkanolamine is diethanolamine.

5. A motor fuel composition according to claim **1** in which said aliphatic alcohol has from about 8 to 12 carbon atoms and said dialkanolamine is diisopropanolamine.

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