

[54] **SLUDGE INHIBITOR FOR HYDROCARBON OILS**

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[58] Field of Search **260/340.2**

[56] **References Cited**

UNITED STATES PATENTS

3,324,033	6/1967	Knapp.....	252/51.5 A
3,340,190	9/1967	Deluga et al.....	252/51.5 A

FOREIGN PATENTS OR APPLICATIONS

1,439,937	4/1966	France
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OTHER PUBLICATIONS

Chemical Abstracts, Vol. 72, (1970), 45778n.

Chemical Abstracts, Vol. 74, (1971), 4220x.

Chemical Abstracts, Vol. 74, (1971), 33334t.

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[57] **ABSTRACT**

A tetrahydric alcohol derived from urea or thiourea and an alkanol amine is esterified with a long chain monocarboxylic acid or dicarboxylic acid, producing an additive that is very effective in reducing the sludging tendencies of hydrocarbon oils. The additive is particularly useful for stabilizing hydrotreated lubricants and fuel stocks against the deposition of sludge when exposed to sunlight.

2 Claims, No Drawings

SLUDGE INHIBITOR FOR HYDROCARBON OILS**BACKGROUND OF THE INVENTION**

Hydrocarbon oils in general, and particularly hydrocarbon oils that have been subjected to treatment in the presence of catalysts tend to form insoluble matter under normal storage conditions. This may first show up as a change in color and a decrease in the clarity of the oil and then subsequently as precipitation of insoluble material in the form of sludge.

Many inhibitors that are effective for preventing the ordinary sludge formation encountered when storing distillate fuels and lubricating oils are not satisfactory for preventing deterioration of mineral lubricating oils and distillate fuels when such oils or fuels are exposed to radiation such as that characteristic of normal sunlight. Oxidation of the lubricating oils and distillate fuels that is initiated by exposure to ultraviolet light is undesirable in that it causes formation of insoluble matter in the oil which will be indicated initially by production of a hazy appearance, and later the formation of sludge.

The tendency of hydrocarbon oils to undergo oxidation when exposed to ultraviolet light and similar sources of actinic radiation is encountered particularly in the case of oils that have been obtained by the hydro-treatment of various hydrocarbon stocks. It is known that improved lubricating properties can be obtained when lubricating oil stocks are treated with hydrogen; such treatment is desirable to produce lubricating stocks for making multigrade lubricants, i.e., those to which suitable viscosity index improvers are added to provide motor oils meeting the SAE 10-40 viscosity specification for example. It appears that upon hydro-treating, the mineral lubricating oils lose some of their naturally occurring oxidation inhibitors that would normally remain to prevent further degradation of the oil upon exposure to sunlight or similar sources of ultraviolet light. There is thus a need for an additive material that will eliminate or at least substantially reduce the tendency of hydrotreated distillate oils to deteriorate when exposed to sunlight.

SUMMARY OF THE INVENTION

It has now been found in accordance with the present invention that petroleum distillate fuels and petroleum lubricating oils that normally tend to become hazy upon exposure to ultraviolet light can be effectively inhibited against such undesirable changes by incorporating into a major amount of the distillate fuel or lubricating oil a small proportion of an ester of a long chain monocarboxylic or dicarboxylic acid and a nitrogen-containing polyhydric alcohol obtained by the condensation of urea or thiourea with an alkanol amine. This additive is superior in its inhibiting power to very closely related esters obtained from the long chain acids and either a polyhydric alcohol such as pentaerythritol or a poly(hydroxyalkyl) alkylene diamine, such as ethylenedinitrilo tetraethanol.

DESCRIPTION OF THE INVENTION

To prepare the esters of this invention, one of the starting materials is a monocarboxylic or dicarboxylic acid or acid anhydride characterized by having a long chain alkyl or alkenyl hydrocarbon group with a total molecular weight in the range of about 500 to about 3500, i.e., the total number of carbon atoms in the hy-

drocarbon groups will be within the range of about 40 to about 250. Preferably, the hydrocarbon groups are derived from a polymer of a C_2 to C_5 monoolefin, e.g., polyethylene, polypropylene or polyisobutylene. Especially useful products are derived from polyisobutylene having a molecular weight within the range of about 800 to about 2500.

A monocarboxylic acid for use in the present invention can be prepared by oxidizing a high molecular weight olefin, e.g., polyisobutylene of about 900 molecular weight, with an oxidizing agent such as nitric acid or oxygen, by preparing an adduct of an aldehyde and an olefin and then oxidizing the adduct, or by halogenating a high molecular weight olefin to form a dihalogen compound and then subjecting the latter to hydrolyzing oxidation. These procedures are taught in British Pat. No. 983,040.

A suitable monocarboxylic acid or derivative thereof can also be obtained by oxidizing a monohydric alcohol with potassium permanganate or by reacting a halogenated high molecular olefin polymer with a ketone. Another convenient method for preparing monocarboxylic acid involves the reaction of metallic sodium with an acetoacetic ester or malonic ester of an alkanol to form a sodium derivative of the ester and the subsequent reaction of the sodium derivative with a halogenated high molecular weight hydrocarbon such as brominated wax or brominated polyisobutylene.

Monocarboxylic acids can also be prepared from olefin polymers such as a polymer of a C_2 to C_5 monoolefin, e.g., polyethylene, polypropylene or polyisobutylene, by halogenating the polyolefin with chlorine or bromine and then condensing it with an unsaturated monocarboxylic acid. Examples of suitable olefin polymers include polyethylene, polypropylene or polyisobutylene, having an average molecular weight of about 350 to 3500, preferably about 800 to 1900. The halogenated polymer is condensed with an alpha, beta-unsaturated, monocarboxylic acid of from 3 to 8 carbon atoms, using at least one mole of acid per mole of halogenated polyolefin. Ordinarily, because of their greater availability, acids of this class having 3 or 4 carbon atoms will be used. Such acids include acrylic acid, alpha-methylacrylic acid (i.e., 2-methyl propenoic acid) and crotonic or isocrotonic acid (beta-methylacrylic acid). Other alpha, beta-unsaturated acids that may be employed include tiglic acid (alpha-methylcrotonic acid), angelic acid (alpha-methylisocrotonic acid), sorbic acid, and cinnamic acid. Additional disclosures regarding the preparation of suitable monocarboxylic acids from halogenated polymers and unsaturated C_3 to C_8 carboxylic acids will be found in the Brewster patent, U.S. Pat. No. 3,489,619, column 3, lines 3 through 70, said disclosure being incorporated herein by reference.

A polycarboxylic acid for use in the invention can be prepared by halogenating a high molecular weight hydrocarbon such as an olefin polymer to produce a polyhalogenated product, converting the polyhalogenated product to a polynitrile, and then hydrolyzing the polynitrile. Polycarboxylic acids can be obtained also by oxidation of a high molecular weight polyhydric alcohol with potassium permanganate, nitric acid, or a like oxidizing agent. Another method for preparing such polycarboxylic acids involves the reaction of an olefin or a polar-substituted hydrocarbon such as a chloropolyisobutylene with an unsaturated polycarbox-

nia rather than ammonia itself, entailing greater expense in its removal.

In the reaction between urea or thiourea and the dialkanol amine, the reaction temperature will be within the range of about 250° and 500°F., preferably 300° to 380°F. Usually, the reaction can be run at atmospheric pressure and the end of the reaction will be determined by cessation of the production of ammonia. Slightly elevated pressures can also be used and the end of the reaction can be determined by a drop in pressure.

The polyalkanol urea obtained as explained above is then esterified with a long chain monocarboxylic or dicarboxylic acid of the nature described above, preferably forming a partial ester of the tetrahydroxy substituted urea, e.g., by reacting 1 mole of the acid with one mole of the substituted urea. In the case of the partial ester of polyisobutenyl succinic anhydride and the substituted urea derived from diethanol amine, the reaction product would be expected to have the following formula the abbreviation PIB designating a polyisobutenyl group:

$$\begin{array}{ccccccc} & & \text{O} & & & & \\ & & \parallel & & & & \\ \text{PIB} - \text{CH} - & \text{C} & - \text{O} - \text{CH}_2\text{CH}_2 & & \text{O} & & \text{CH}_2\text{CH}_2\text{OH} \\ & | & & \diagdown & \parallel & \diagup & \\ & \text{CH}_2 - \text{C} & - \text{O} - \text{CH}_2\text{CH}_2 & & \text{N} - \text{C} - \text{N} & & \\ & \parallel & & \diagup & & \diagdown & \\ & \text{O} & & & & & \text{CH}_2\text{CH}_2\text{OH} \end{array}$$

Since the substituted urea or thiourea has four hydroxy groups it is possible to esterify one, two, three, or all four of such groups by varying the proportion of acid to hydroxy compound. Also, in the case of a dibasic acid such as succinic acid it is possible to esterify only one of the carboxy groups. It is preferred in this invention to esterify two of the four hydroxy groups of the substituted urea, which in the case of a dicarboxylic

acid involves 1 molar proportion of dicarboxylic acid, or 2 molar proportions of monocarboxylic acid, per mole of the tetrahydric alcohol substituted urea. Mixtures of esters are also within the contemplation of the invention.

60 The esterification reaction can involve any standard procedure that is normally used in the preparation of a carboxylic acid ester. The reaction temperatures will generally be in the range of about 200° to 500°F., more
65 usually about 250° and 450°F. The esterification can be promoted with a conventional catalyst such as sulfuric acid, benzene sulfonic acid, paratoluene sulfonic acid, and the like. Effective concentrations of catalysts will

usually about 250° and 450°F. The esterification can be promoted with a conventional catalyst such as sulfuric acid, benzene sulfonic acid, paratoluene sulfonic acid, and the like. Effective concentrations of catalysts will

In place of urea or thiourea, one could also use a substituted urea or thiourea, although normally there would be no economic advantage in doing so because the reaction byproduct would be a substituted ammo-

range from about 0.01 to about 3% by weight based on the total weight of the reaction mixture. Completion of the esterification reaction can be determined in the conventional manner which usually involves measuring the amount of water evolved in the reaction. If desired, the esterification process can be conducted in the presence of a substantially inert organic diluent, preferably one that will form an azeotrope with water to assist in the removal of water from the reaction mixture. The esterification reaction can also be conducted in the presence of a lubricating oil diluent, which will facilitate the reaction by reducing the viscosity of the reaction mixture. Moreover, when this is done the product is obtained in the form of a concentrate containing for example, 40 to 50% additive, which will facilitate blending of the additive into the finished lubricating oil composition.

The additives of this invention will be employed in concentrations ranging from about 0.001 to about 10 weight percent in oil compositions ranging from gasoline fractions through middle distillate fuels and lubricating oils.

For use as lubricating oil additives the reaction products of this invention can be incorporated in lubricating oil compositions in concentrations within the range of from about 0.1 to about 10 weight percent and will ordinarily be used in concentrations of from about 0.1 to about 2 weight percent. The lubricating oils to which the additives of the invention can be added include not only mineral lubricating oils, but synthetic oils also. The mineral lubricating oils may be of any preferred types, including those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods.

The additives of this invention can also be employed in middle distillate fuels for inhibiting corrosion and the formation of a sludge and sediment in such fuels. Concentration ranges of from about 0.001 to about 2 weight percent, or more generally from about 0.005 to about 0.2 weight percent are employed. Petroleum distillate fuels boiling in the range of from about 300° to about 900°F. are contemplated. Typical of such fuels are No. 1 and No. 2 fuel oils that meet ASTM Specification D-396-48T, diesel fuels qualifying as Grades 1D, 2D and 4D of ASTM Specification D-972-51T, and various jet engine fuels.

The additives of this invention are especially useful in mineral lubricating oils or mineral distillate fuels that have been treated with hydrogen, particularly those that have been subjected to a severe hydrotreating or hydrocracking process. See J. B. Gilbert and J. Walker, "Manufacture of Lubricating Oils by Hydrocracking," Eighth World Petroleum Congress Proceedings, Vol. 4, pages 147-158 (Applied Science Publishers, London, 1971).

In either the fuel or lubricating compositions, other conventional additives can also be present including oiliness and extreme pressure agents, dyes, corrosion inhibitors, foam suppressants, viscosity index improvers, and the like.

The additives of this invention will not only be used in finished lubricant or fuel compositions but also as additive concentrates. Such concentrates can contain from about 10 to about 80 weight % of additive on an active ingredient basis, the balance being hydrocarbon oil, e.g., lubricating oil or fuel. Such concentrates are convenient for handling the additive when conducting

the ultimate blending operation to prepare the finished lubricating oil or fuel composition.

The nature of this invention will be further understood when reference is made to the following examples, which include preferred embodiments.

EXAMPLE I

Polyisobutenyl succinic anhydride was prepared by reaction of polyisobutylene of about 900 molecular weight with maleic anhydride. One mole of urea was mixed with two moles of diethanol amine and the mixture was heated at 330°-350°F., with stirring until evolution of ammonia ceased. Then one mole of the resulting substituted urea was mixed with one mole of the polyisobutenyl succinic anhydride, and the mixture was heated at 300°F. in the presence of a catalytic amount of paratoluene sulfonic acid, the reaction being conducted over a period of several hours while a stream of nitrogen was bubbled through the mixture. A clear oil-soluble product was obtained.

For purposes of comparison, a separate portion of the polyisobutenyl succinic anhydride was esterified in like manner with 1 mole of ethylene dinitrilo tetraethanol, EDTE, which is also known as N,N,N',N'-tetrakis (2-hydroxyethyl) alkylene diamine.

To test the effectiveness of an additive of the invention in inhibiting sludge caused by ultraviolet light, a blend was prepared by adding 0.1% of the substituted urea ester prepared as described above to a hydrocracked lubricating oil. Comparative blends were prepared by blending respectively 0.1 weight % of the EDTE ester described above in the same hydrocracked oil, and 0.1 weight % of the diester of polyisobutenyl succinic anhydride and pentaerythritol (PIBSA/PE) to another portion of the hydrocracked oil. The latter was in the form of a 50 weight % concentrate in a mineral lubricating oil; sufficient of the concentrate was used to furnish 0.1 wt. % of actual additive in the blend.

Each of the blends was subjected to ultraviolet radiation by the following procedure. A sample of the blend in a 4 oz. sample bottle is placed 12 inches from a 275 watt ultraviolet sunlamp. To ensure reproducibility of the tests the lamps in the test apparatus are replaced every 1000 hours. The bottle contains 96 ml. of oil and is fitted with a slotted stopper to allow access of air. The number of days required to first form precipitated sludge in the test for each sample is noted. A control test is run on a sample of the hydrocracked oil without any additive. The results obtained in the ultraviolet radiation tests are shown in Table I which follows. The range of values in replicate tests is given in each instance.

TABLE I

ADDITIVE	DAYS TO FORM SLUDGE IN ULTRAVIOLET LIGHT
None	1 - 2
Additive of Invention	14 - 17
EDTE Ester	4 - 5
PIBSA/PE	4 - 5

It will be noted that the ester of the present invention was much more effective than either of the comparative esters in preventing sludging in the presence of ultraviolet light.

The hydrocracked lubricating oil used in the tests was a hydrocracked dewaxed oil originating from an

Arabian crude oil. It had an API gravity of 34.8°, a viscosity of 49.4 SUS at 210°F., an ASTM D567 viscosity index of 125.5, a pour point of 0°F. and a Conradson carbon value of 0.02.

EXAMPLE 2

As an added example of the preparation of an additive of the invention, two moles of diisopropanol amine is reacted with one mole of urea as in Example 1; then one mole of the resulting tetrahydric alcohol substituted urea is reacted with two moles of polyisobutenyl propionic acid, the latter being dissolved in an equal volume of a solvent refined lubricating oil having a viscosity of 150 SUS at 100°F. Esterification is conducted for several hours at 340°F., yielding a concentrate of the desired ester suitable for blending into a finished lubricant.

The polyisobutenyl propionic acid used in this example has been prepared by chlorinating polyisobutylene of 780 molecular weight to 4.3 wt. % chlorine content, reacting about 11 parts by weight of the chlorinated product with 1 part by weight of acrylic acid at 425°F.

for about 6 hours at 20 psig, followed by nitrogen purging to remove unreacted acrylic acid.

Although this invention has been described in its preferred forms with a certain degree of particularity, it is to be understood that numerous modifications and adaptations can be resorted to without departing from the spirit of the invention or from its scope as defined in the appended claims.

What is claimed is:

- 10 1. The oil-soluble ester obtained by the esterification of about equal molar proportions of (a) a polyisobutenyl succinic acid or acid anhydride wherein said polyisobutenyl group contains between 40 and 250 carbon atoms with (b) a tetrahydroxyalkyl-substituted urea which is the condensation product of 1 molar proportion of urea with about 2 molar proportions of a di-
15 alkanolamine having from 1 to 6 carbon atoms in each alkanol group.
- 20 2. The ester of claim 1 wherein said polyisobutenyl group is derived from a polyisobutylene of 800 to 2100 molecular weight.

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