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HYDROCARBON OIL COMPOSITION

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This invention relates to a novel additive for hydrocarbon oil and more particularly to a novel method of improving hydrocarbon oil in a number of important properties.

During processing, transportation, storage and/or use, hydrocarbon oils generally deteriorate, particularly when subjected to elevated temperature. For example, hydrocarbon oil being subjected to fractionation or conversion is first heated to an elevated temperature. Such heating may be effected in an externally fired furnace or it may be accomplished by heat exchange with a hotter fluid. In the first case, the hydrocarbon fluid is passed through tubes during such heating and, in many cases, deposit formation occurs in the tubes and results in loss of efficient heating and/or plugging of the furnace tubes. In heat exchange systems the hydrocarbon oil is passed either through tubes disposed in a shell or through the shell surrounding the tubes. During heating of the oil, deposit formation occurs either within the tubes or in the hotter sections of the shell, with the result of decreased efficiency in heat transfer and even in plugging of the tubes. Another example in which hydrocarbon oil is passed in heat exchange is in the case of jet fuel, where the jet fuel is passed in heat exchange with the hot exhaust gases, both to cool the exhaust gases and to heat the incoming fuel. Temperatures as high as 500° F. or more are encountered for at least short periods of time, with the result that deposit formation occurs and either plugs the heat exchanger or interferes with efficient heat transfer.

Other examples where instability of the hydrocarbon oil is a problem are hydrocarbon oils heavier than gasoline including diesel oil, heater oils, burner oils, range oils, fuel oils, transformer oils, hydraulic oils, slushing oils, etc. Deposit formation in these oils is objectionable because it results in plugging of filters, strainers, burner tips, injectors, etc., reduction in viscosity and accordingly in flowing properties, as well as the formation of varnish and sludge in the diesel engine. In addition to preventing these objectionable deposit formations, the novel additive of the present invention also functions to retard corrosion of metal surfaces in contact with hydrocarbon oil and water. It is well known that water generally is present in hydrocarbon oils and results in corrosion of piping, pumps, shells, fractionators, receivers, storage tanks, etc., as well as internal equipment such as baffle plates, bubble trays, bubble caps, etc.

In addition to serving the important functions hereinbefore set forth, the novel additive of the present invention also serves to lower the pour point of the hydrocarbon oil. This is of advantage in the case of heavier oils which are being pumped and also of particular advantage in the case of lubricating oils, gas turbine oils, steam turbine oils, jet turbine oils, marine oils, etc. in order that the oil retain its flowing properties at lower temperatures. In addition to reducing pour point and lowering the cold test, the additive also improves the viscosity index of lubricating oil.

The additive of the present invention also serves an important function in the case of gasoline or naphtha. As hereinbefore set forth, the additive serves as a corrosion inhibitor and therefore reduces corrosion problems during handling of the gasoline.

The additive also serves to improve hydrocarbon oils in another important manner. In many instances hydro-

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carbon oil must meet water tolerance specifications. According to these specifications, a mixture of isooctane or jet fuel, water and the additive is shaken for a short period of time and then allowed to stand for a given time. After this time there must be a clear break in order for the oil to pass this test. As will be shown in the appended example, the additive of the present invention is especially advantageous in permitting the hydrocarbon oil to pass this test.

From the above description it will be noted that the novel additive of the present invention serves to improve hydrocarbon oil in a number of different ways. The hydrocarbon oil includes gasoline, naphtha, jet fuel, kerosene, burner oil, heater oil, range oil, gas oil, fuel oil, lubricating oil, residual oil, etc. As hereinbefore set forth, the additive may be incorporated in the oil prior to heating for further processing, or it may be incorporated in the oil after such treatment.

In one embodiment the present invention relates to a method of improving a hydrocarbon oil which comprises incorporating therein a stabilizing concentration of an ester of a carboxylic acid and the condensation product of an epihalohydrin compound with an amine compound having at least 12 carbon atoms.

In a specific embodiment the present invention relates to a method of preventing deposit formation in a heat exchanger through which two fluids at different temperatures are passed which comprises incorporating in at least one of said fluids, in an amount sufficient to prevent deposit formation, an ester of oleic acid and the condensation product of epichlorohydrin with an amine compound having from about 12 to about 40 carbon atoms per molecule.

In still another embodiment the present invention relates to a method of improving burner oil which comprises incorporating therein a stabilizing concentration of an ester of the reaction product of terpene-maleic anhydride and the condensation product of epichlorohydrin and tallow amine.

In still another embodiment the present invention relates to hydrocarbon oil containing a stabilizing concentration of the novel additive herein set forth.

The novel additives of the present invention also are new compositions of matter and are being so claimed in the present application.

As hereinbefore set forth, the novel additive of the present invention is an ester of a carboxylic acid and the condensation product of an epihalohydrin compound with an amine compound having at least 12 carbon atoms. The amine compound used in preparing the condensation product contains at least 12 carbon atoms and preferably at least 15 carbon atoms. Generally the total number of carbon atoms in the amine will not exceed about 40 carbon atoms per molecule. In a preferred embodiment the amine contains a straight chain of at least 3 carbon atoms attached to the nitrogen atom. In this preferred embodiment, the alkyl group attached to the nitrogen atom is of normal configuration and not secondary, tertiary or of cyclic configuration. However, the alkyl group may contain branching in the chain, provided such branching occurs on the fourth carbon atom from the nitrogen atom or further distant therefrom.

Any suitable alkyl amine meeting the requirements set forth herein may be used in preparing the additive of the present invention. In addition to the above requirements, it is essential that the alkyl amine is a primary or secondary amine; that is, only one or two of the hydrogen atoms attached to the nitrogen atom are substituted by alkyl groups. Tertiary amines (no hydrogen atom attached to the nitrogen atom) cannot be used in the present invention. It is understood that the term "alkyl amine" is used in the present specifications and claims

to include primary alkyl amines, secondary alkyl amines, polyamines, N-alkyl polyamines, N,N'-dialkyl polyamines, etc., all of which meet the requirements hereinbefore set forth.

Illustrative examples of primary alkyl amines include dodecyl amine, tridecyl amine, tetradecyl amine, pentadecyl amine, hexadecyl amine, heptadecyl amine, octadecyl amine, nonadecyl amine, eicosyl amine, heneicosyl amine, docosyl amine, tricosyl amine, tetracosyl amine, pentacosyl amine, hexacosyl amine, heptacosyl amine, octacosyl amine, nonacosyl amine, triacontyl amine, hentriacontyl amine, dotriacontyl amine, tritriacontyl amine, tetratriacontyl amine, pentatriacontyl amine, hexatriacontyl amine, heptatriacontyl amine, octatriacontyl amine, nonatriacontyl amine, tetracontyl amine, etc. Conveniently the long chain amines are prepared from fatty acids or more particularly from mixtures of fatty acids formed as products or by-products. Such mixtures are available commercially, generally at lower prices and, as another advantage of the present invention, the mixtures may be used without the necessity of separating individual amines in pure state.

An example of such a mixture is hydrogenated tallow amine which is available under various trade names including "Alamine H26D" and "Armeen HTD." These products comprise mixtures predominating in alkyl amines containing 6 to 18 carbon atoms per alkyl group, although they contain a small amount of alkyl groups having 14 carbon atoms, and also meet the other requirements hereinbefore set forth.

Illustrative examples of secondary amines include di-(dodecyl) amine, di-(tridecyl) amine, di-(tetradecyl) amine, di-(pentadecyl) amine, di-(hexadecyl) amine, di-(heptadecyl) amine, di-(octadecyl) amine, di-(nonadecyl) amine, di-(eicosyl) amine, etc. In another embodiment, which is not necessarily equivalent, the secondary amine will contain one alkyl group having at least 12 carbon atoms and another alkyl group having less than 12 carbon atoms, both of the alkyl groups having a straight chain of at least 3 carbon atoms attached to the nitrogen atom. Illustrative examples of such compounds include N-propyl-dodecyl amine, N-butyl-dodecyl amine, N-amyl-dodecyl amine, N-butyl-tridecyl amine, N-amyl-tridecyl amine, etc. Here again, mixtures of secondary amines are available commercially, usually at a lower price, and such mixtures may be used in accordance with the present invention, provided that the amines meet the requirements hereinbefore set forth. An example of such a mixture available commercially in "Armeen 2HT" which consists primarily of dioctadecyl amine and dihexadecyl amine.

Preferred examples of N-alkyl polyamines comprise N-alkyl-1,3-diaminopropanes in which the alkyl group contains at least 12 carbon atoms. Illustrative examples include N-dodecyl-1,3-diaminopropane, N-tridecyl-1,3-diaminopropane, N-tetradecyl-1,3-diaminopropane, N-pentadecyl-1,3-diaminopropane, N-hexadecyl-1,3-diaminopropane, N-heptadecyl-1,3-diaminopropane, N-octadecyl-1,3-diaminopropane, N-nonadecyl-1,3-diaminopropane, N-eicosyl-1,3-diaminopropane, N-heneicosyl-1,3-diaminopropane, N-docosyl-1,3-diaminopropane, N-tricosyl-1,3-diaminopropane, N-tetracosyl-1,3-diaminopropane, N-pentacosyl-1,3-diaminopropane, N-hexacosyl-1,3-diaminopropane, N-heptacosyl-1,3-diaminopropane, N-octacosyl-1,3-diaminopropane, N-nonacosyl-1,3-diaminopropane, N-triacontyl-1,3-diaminopropane, N-hentriacontyl-1,3-diaminopropane, N-dotriacontyl-1,3-diaminopropane, N-tritriacontyl-1,3-diaminopropane, N-tetratriacontyl-1,3-diaminopropane, N-pentatriacontyl-1,3-diaminopropane, N-hexatriacontyl-1,3-diaminopropane, N-heptatriacontyl-1,3-diaminopropane, N-octatriacontyl-1,3-diaminopropane, N-nonatriacontyl-1,3-diaminopropane, N-tetracontyl-1,3-diaminopropane, etc. As before, mixtures are available commercially, usually at lower prices, of suit-

able compounds in this class and advantageously are used for the purposes of the present invention. One such mixture is "Duomeen T" which is N-tallow-1,3-diaminopropane and predominates in alkyl groups containing 16 to 18 carbon atoms each, although the mixture contains a small amount of alkyl groups containing 14 carbon atoms each. Another mixture available commercially is N-coco-1,3-diaminopropane which contains alkyl groups predominating in 12 to 14 carbon atoms each. Still another example is N-soya-1,3-diaminopropane which predominates in alkyl groups containing 18 carbon atoms per group, although it contains a small amount of alkyl groups having 16 carbon atoms.

While the N-alkyl-1,3-diaminopropanes are preferred compounds of this class, it is understood that suitable N-alkyl ethylene diamines, N-alkyl-1,3-diaminobutanes, N-alkyl-1,4-diaminobutanes, N-alkyl-1,3-diaminopentanes, N-alkyl-1,4-diaminopentanes, N-alkyl-1,5-diaminopentanes, N-alkyl-1,3-diaminohexanes, N-alkyl-1,4-diaminohexanes, N-alkyl-1,5-diaminohexanes, N-alkyl-1,6-diaminohexanes, etc. may be employed but not necessarily with equivalent results. Also, it is understood that polyamines containing 3 or more nitrogen atoms may be employed provided they meet the requirements hereinbefore set forth. Illustrative examples of such compounds include N-dodecyl-diethylene triamine, N-tridecyl-diethylene triamine, N-tetradecyl-diethylene triamine, etc., N-dodecyl-dipropylene triamine, N-tridecyl-dipropylene triamine, N-tetradecyl-dipropylene triamine, etc., N-dodecyl-dibutylene triamine, N-tridecyl-dibutylene triamine, N-tetradecyl-dibutylene triamine, etc., N-dodecyl-triethylene tetramine, N-tridecyl-triethylene tetramine, N-tetradecyl-triethylene tetramine, etc., N-dodecyl-tripropylene tetramine, N-tridecyl-tripropylene tetramine, N-tetradecyl-tripropylene tetramine, etc., N-dodecyl-tributylene tetramine, N-tridecyl-tributylene tetramine, N-tetradecyl-tributylene tetramine, etc., N-dodecyl-tetraethylene pentamine, N-tridecyl-tetraethylene pentamine, N-tetradecyl-tetraethylene pentamine, etc., N-dodecyl-tetrapropylene pentamine, N-tridecyl-tetrapropylene pentamine, N-tetradecyl-tetrapropylene pentamine, etc., N-dodecyl-tetrabutylene pentamine, N-tridecyl-tetrabutylene pentamine, N-tetradecyl-tetrabutylene pentamine, etc.

In another embodiment, polyaminoalkanes meeting the requirements hereinbefore set forth, may be employed but generally such materials are not available commercially and, therefore, generally are not preferred. Illustrative examples of such compounds include 1,12-diaminododecane, 1,13-diaminotridecane, 1,14-diaminotetradecane, etc.

In general, it is preferred that the amine compound is a saturated compound and does not contain double bonds in the chain. However, in some cases, unsaturated compounds may be employed, provided they meet the other requirements hereinbefore set forth, although not necessarily with equivalent results. Such amine compounds may be prepared from unsaturated fatty acids and, therefore, may be available commercially at lower cost. Illustrative examples of such amine compounds include dodecylenic amine, didodecylenic amine, N-dodecylenic ethylene diamine, N-dodecylenic-1,3-diaminopropane, oleic amine, dioleic amine, N-oleic ethylene diamine, N-oleic-1,3-diaminopropane, linoleic amine, dilinoleic amine, N-linoleic ethylene diamine, N-linoleic-1,3-diaminopropane, etc. It is understood that these amine compounds are included in the present specifications and claims by reference to amine or amine compounds.

In another embodiment of the invention, two different amines may be reacted with the epihalohydrin compound. At least one of the amines must meet the qualifications hereinbefore set forth. The other amine may comprise any suitable compound containing primary and/or secondary amine groups. Preferred compounds comprise ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, etc., similar propylene and polypropylene polyamines, butylene and poly-

least 6 carbon atoms per molecule are preferred. However, it is understood that dibasic acids containing less than 6 carbon atoms also may be employed in some cases and thus include oxalic, malonic, succinic, glutaric, etc.

In another embodiment, the carboxylic acid used in forming the ester is a reaction product of a terpene and an alpha,beta-unsaturated carboxylic acid or anhydride. Any suitable terpenic compound may be reacted with any suitable alpha-beta-unsaturated polycarboxylic acid or anhydride to form the reaction product for subsequent condensation with the epichlorohydrin-amine condensation product. In one embodiment a terpene hydrocarbon having the formula $C_{10}H_{16}$ is employed, including alpha-pinene, beta-pinene, dipentane, d-limonene, 1-limonene and terpinoline. These terpene hydrocarbons have boiling points ranging from about 150° to about 185° C. In another embodiment the terpene may contain three double bonds in monomeric form, including terpene as allo-o-cymene, o-cymene, myrcene, etc. Other terpenic compounds include alpha-terpinene, p-cymene, etc.

As hereinbefore set forth, the terpene is reacted with an alpha,beta-unsaturated polycarboxylic acid or anhydride thereof. Any unsaturated polycarboxylic acid having a point of unsaturation between the alpha and beta carbon atoms may be employed. Illustrative unsaturated dicarboxylic acids include maleic acid, fumaric acid, citraconic acid, mesaconic acid, aconitic acid, itaconic acid. While the dicarboxylic acids are preferred, it is understood that alpha,beta unsaturated polycarboxylic acids containing three, four or more carboxylic acid groups may be employed. Furthermore, it is understood that a mixture of alpha-beta-unsaturated polycarboxylic acids and particularly of alpha,beta-unsaturated dicarboxylic acids may be used.

While the alpha,beta-unsaturated polycarboxylic acid may be employed, advantages appear to be obtained in some cases when using the anhydrides thereof. Illustrative anhydrides include maleic anhydride, citraconic anhydride, aconitic anhydride, itaconic anhydride, etc. It is understood that a mixture of anhydrides may be employed and also that the anhydride may contain substituents and particularly hydrocarbon groups attached thereto.

The reaction of terpene and alpha,beta-unsaturated acid or anhydride generally is effected at a temperature of from about 150° to about 300° C., and preferably of from about 160° to about 200° C. The time of heating will depend upon the particular reactants and may range from 2 hours to 24 hours or more. When desired, a suitable solvent may be utilized. Following the reaction, impurities or unreacted materials may be removed by vacuum distillation or otherwise, to leave a resinous product which may be a viscous liquid or a solid.

A terpene-maleic anhydride reaction product is available commercially under the trade name of "Petrex acid." This acid is a stringy, yellow-amber colored mass and is mostly dibasic. It has an acid number of approximately 530, a molecular weight of approximately 215 and a softening point of 40°-50° C.

While the aliphatic carboxylic acids generally are preferred, in some cases cyclic carboxylic acids may be employed. Aromatic carboxylic acids include benzoic acid, toluic acid, etc., which acids also may contain hydrocarbon and particularly alkyl substituents attached to the ring. Naphthenic carboxylic acids include cyclopentane carboxylic acid; cyclopentyl-acetic acid, methylcyclopentyl acid, camphanic acid, cyclohexane carboxylic acid, methylcyclohexane carboxylic acid, dimethylcyclohexane carboxylic acid, trimethylcyclohexane carboxylic acid, etc.

It is understood that the various acids which may be used in preparing the ester are not necessarily equivalent and also that mixtures of acids may be employed in preparing the esters. In some cases, in place of the acid, the anhydrides or certain esters of the acid may be utilized

in forming the ester with the condensation product of epihalohydrin-amine. These esters may contain up to about 8 carbon atoms in the ester group but preferably contain one or two carbon atoms. The ester portion must be volatile under the conditions of the esterification of the epihalohydrin-amine condensation product. In the esterification of the condensation product, transesterification occurs; that is, the smaller ester group is volatilized off and replaced by esterification of the epihalohydrin-amine condensation product.

The ester of the carboxylic acid and epihalohydrin-amine condensation product may comprise the partially or completely esterified product. As hereinbefore set forth, the epihalohydrin-amine condensation product may and preferably contains a number of recurring units, each of the recurring units having a hydroxyl group. Accordingly, it will be seen that one, all or any number of the hydroxyl groups may be esterified with the acid. Generally it is preferred to use stoichiometric amounts of these reactants in order to effect substantially complete esterification. One mol equivalent of carboxylic acid will be used per each equivalent of hydroxyl group in the epihalohydrin-amine condensation product.

The ester may be prepared in any suitable manner and, in general, is prepared readily by refluxing the acid and condensation product, preferably with the continuous removal of water formed in the reaction. The refluxing is continued until the theoretical amount of water is collected and thus may range from 1 hour to 48 hours or more at a temperature above about 80° C. Although the esterification may be effected in the absence of a solvent, which generally will require the use of vacuum, normally it is preferred to utilize a solvent. The exact temperature or refluxing will depend upon the particular solvent employed. For example, with benzene as the solvent, the temperature will be in the order of 80° C., with toluene the temperature will be in the order of 120° C., and with xylene in the order of 150°-155° C. Other preferred solvents include cumene, naphtha, decalin, etc. Any suitable amount of the solvent may be employed but preferably should not comprise a large excess because this will tend to lower the reaction temperature and slow the reaction. Water formed during the reaction may be removed in any suitable manner including, for example, by operating under reduced pressure, by removing an azeotrope of water-solvent, by distilling the condensation product at an elevated temperature, etc. As hereinbefore set forth, a higher temperature and solvent preferably are utilized in effecting the reaction in order to remove the water as it is being formed.

It is understood that the different esters which may be prepared and used in accordance with the present invention are not necessarily equivalent. For example, one ester may be effective for a certain purpose in one hydrocarbon oil, while another ester may be effective in the same substrate for a different purpose or in different substrates for the same or different purposes.

The concentration of esters to be incorporated in the hydrocarbon oil will depend upon the particular use. For example, when utilized to prevent heat exchanger deposits, the ester generally is used in a concentration of from 1 to 1000 parts per million by weight of the hydrocarbon oil. When used for other purposes, the ester may be used in a concentration of from about 0.0001% to about 1% or more by weight of the hydrocarbon oil. It is understood that the ester is incorporated in the hydrocarbon oil in any suitable manner and generally is effected with stirring in order to obtain intimate mixing thereof. However, when introduced in a flowing stream of oil, mixing is accomplished by turbulence normally encountered therein.

As hereinbefore set forth, the ester is particularly advantageous for use to prevent deposit formation in heat exchangers. Such heat exchange is utilized, for example, in a hydrotreating process in which oil is subjected to

hydrogen treating in the presence of a catalyst comprising alumina-molybdenum oxide-cobalt oxide or alumina-molybdenum sulfide-cobalt sulfide. The oil, which may comprise gasoline, kerosene, gas oil or mixtures thereof, is introduced into the process at a temperature of from about ambient to 200° F. and is passed in heat exchange with reactor effluent products being withdrawn at a temperature of from about 500° to about 800° F. The charge is heated by such heat exchange to a temperature of from about 300° to about 600° F., then is heated in a furnace or otherwise to a temperature of from about 625° to about 800° F. and passed with hydrogen in contact with the catalyst. This treatment serves to remove impurities and to hydrogenate unsaturates contained in the charge. Another illustration is a reforming process in which gasoline is contacted with hydrogen in the presence of a platinum-containing catalyst at a temperature of from about 700° to about 1000° F. and the hot effluent product from the reaction zone is passed in contact with the charge in order to cool the former and heat the latter.

An example in which oil is subjected to fractionation and the charge is passed in heat exchange with the hot effluent products is in a crude column. In this column, crude oil is subjected to distillation at a temperature of from about 600° to about 700° F. in order to remove lighter components as overhead and/or side streams. In some cases the charge first is passed in heat exchange with the overhead and/or side streams from this column and then is passed in heat exchange with the hotter products withdrawn from the bottom of the crude column. In this way the charge is progressively heated and the hotter products are cooled.

The above examples are illustrative of typical uses of heat exchange to effect economies in the process. However, difficulty is experienced in the heat exchange due to deposit formation, with the consequent necessity of interrupting plant operation as hereinbefore set forth. In accordance with the present invention, deposit formation in heat exchanger is reduced to an extent that normal plant operation need not be interrupted for this reason.

It is understood that the advantages of the present invention may be obtained in any suitable heat exchange equipment. In general, this equipment comprises a series of tubes or a tube coil positioned within a shell. One of the fluids is passed through the tubes, while the other fluid is passed through the shell. The heat exchange equipment generally is positioned externally to a fractionator or reactor. However, in some cases, the heat exchanger takes the form of a reboiler or condenser, and either a tube coil or a shell containing tubes is positioned within the lower or upper portion of the fractionator or reactor.

When the ester of the present invention is added to a finished product, it is incorporated therein with suitable mixing, and may be used along with other additives to be added to the oil for specific reasons as, for example, metal deactivator, antioxidant, synergist, cetane improver, etc. As hereinbefore set forth, the ester serves to improve the oil in many ways including preventing deposition of sediment, preventing formation of varnish or sludge, preventing corrosion of metal surfaces, depressing pour point, etc. It is understood that all of these improvements are not necessarily obtained in all substrates with the same additive. However, the different oils will be improved in one or more ways as hereinbefore set forth.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

The ester of this example is the 2-ethylhexoic acid ester of the condensation product of epichlorohydrin and tallow amine. The condensation product was prepared by the reaction of equal mol proportions of hydrogenated

tallow amine (Armeen HTD) and epichlorohydrin. It will be noted that the tallow amine is a mixture of primary amines predominating in 16 to 18 carbon atoms per alkyl group. The reaction was effected by first forming a solution of 2 mols of epichlorohydrin in 600 cc. of a solvent mixture comprising 400 cc. of xylene and 200 cc. of 2-propanol. A separate solution of 2 mols of Armeen HTD was prepared in an equal volume of xylene. One mol of the latter solution was added gradually to the epichlorohydrin solution, with stirring and heating at 55°–60° C. for a period of 2.5 hours. Then another mol of Armeen HTD was added gradually to the reaction mixture, stirred and reacted at 80° C. for 2.5 hours. One mol of sodium hydroxide then was added with stirring and heating at 85°–90° C. for 3.5 hours, after which another mol of sodium hydroxide was added and the mixture stirred and reacted at 85°–90° C. for one hour. Following completion of the reaction, the mixture was cooled, filtered, and the filtrate then was distilled to remove the alcohol. The condensation product was recovered as a 50% by weight solution of active ingredient in xylene.

330 grams of the 50% solution of the condensation product prepared in the above manner was mixed with 75 grams of 2-ethylhexoic acid. The condensation product was used in a ½ equivalent of the hydroxyl groups and the ethylhexoic acid was used in a concentration of ½ mol. The mixture was boiled under refluxing conditions for 24 hours. A total of 20.8 cc. of water was collected. The xylene was removed by distillation on a steam bath under vacuum. The ester was recovered as a dark brown, free-flowing liquid and had an index of refraction n_D^{20} of 1.4693.

The ester prepared in the above manner was evaluated in a method referred to as the "Erdco test." In this method heated oil is passed through a filter, and the time required to develop a pressure differential across the filter of 25 in./Hg is determined. It is apparent that the longer the time required to reach this differential pressure, the more effective is the additive.

The oil used in this example was a mixture of 76% range oil and 24% catalytically cracked cycle oil. When evaluated in the Erdco test using a preheater temperature of 300° F. and a filter temperature of 350° F., a sample of the oil not containing an additive developed 25 in./Hg pressure within 35 minutes. On the other hand, another sample of the oil containing 0.0001% by weight of the ester described above and evaluated in the same manner developed a differential pressure of only 0.5 in./Hg after 180 minutes. It will be seen that this low concentration of additive was effective in considerably reducing filter plugging.

EXAMPLE II

The ester of this example was prepared using a mixed fatty acid which is available in the open market as "Neo-Fat 18–55" and contains 49% stearic acid, 48% palmitic acid and 3% oleic acid. It is apparent that the resultant product is a mixed ester. However, it also is apparent that these mixed acids are available commercially at a lower price than the pure acids. As another important feature of the present invention, these mixed acids are used to prepare the ester without the additional cost otherwise required to separate and recover the pure acid.

165 grams of a condensation product (50% solution in xylene) prepared in the manner described in Example I is commingled with 67 grams of the mixed acid. The condensation product is used in a concentration of ¼ equivalent of the hydroxyl groups and the mixed acid is used in a concentration equivalent to ¼ mol. The mixture was boiled at refluxing conditions (temperature 150°–155° C.) for 16 hours. 8 cc. of water was collected. Xylene was removed by distillation on a steam bath under vacuum. The ester was recovered as an amber, brittle solid, having a melting point of 48°–53° C.,

and is readily soluble in hydrocarbon oil at slightly elevated temperature.

The ester prepared in the above manner was evaluated in the Erdco test using another sample of the oil described in Example I. The preheater temperature was 300° F. and the filter temperature was 350° F. 0.0005% by weight of the ester prepared in the above manner was incorporated into another sample of the oil described in Example I, and developed a differential pressure of only 0.1 in./Hg after 180 minutes. This is to be compared to the 25 in./Hg pressure developed in 35 minutes when using the oil without additive. Here again it will be noted that the additive of the present invention was effective in retarding filter plugging.

EXAMPLE III

The ester of this example was prepared using a mixed acid available commercially as "Neo-Fat 94-04." This mixed acid comprises 80% oleic acid, 10% linoleic acid, 5% stearic acid, 4% palmitic acid and 1% linolenic acid. As mentioned before, it is an important advantage of the present invention that these mixed acids are used satisfactorily to prepare effective additives without the additional cost otherwise necessary to separate substantially pure acids.

163.1 grams of a condensation product (50% solution in xylene) prepared in the manner described in Example I was commingled with 70.5 grams of the mixed acid described above, together with 100 grams of xylene, and the mixture was refluxed at 148° C. The condensation product was used in a concentration of ¼ equivalent based on hydroxyl content and the mixed acid was used in a concentration of ¼ mol. Following completion of the reaction, the product was heated to 170° C. under water pump vacuum to remove the xylene. The product was recovered as a grainy solid which became fluid at temperatures above 80° F. It had a basic nitrogen content of 1.54 meq./g. and an acid number of 0.38 meq./g. The index of refraction n_D^{20} is 1.4785.

The ester prepared in the above manner was used as a pour point depressant in lubricating oil, which lubricating oil was a commercial S.A.E. 20 Mid-Continent solvent extracted oil. This oil, without additive, had an ASTM cold test of 5° F. and an ASTM pour point of 10° F. 1% by weight of the ester prepared in the above manner was incorporated in a sample of this lubricating oil and served to reduce the ASTM cold test to -5° F. and the ASTM pour point to 0° F.

EXAMPLE IV

The ester prepared as described in Example II also was evaluated in the Erdco test. In this run a commercial J.P.-6 jet fuel was used and accordingly was evaluated at a higher temperature. This is because jet fuels normally encounter higher temperatures during use. In this run the preheater is at a temperature of 400° F. and the filter at a temperature of 500° F. Furthermore, the particular jet fuel used in this run was extremely difficult to benefit by an additive. Several commercially available and normally effective experimental additives were evaluated in this jet fuel and were of no benefit. Accordingly, the improved results obtained with the ester of this example is evidence of the unusual effectiveness of this additive.

The J.P.-6 jet fuel without additive developed a differential pressure of 25 in./Hg within 117 hours. 0.005% by weight of the ester described in Example III was incorporated in another sample of this fuel, and the fuel developed a differential pressure of only 0.65 in./Hg after 300 minutes.

The ester also was evaluated according to the C.F.R. fuel coker thermal stability test. In this test, the oil heated to the specified temperature is passed through the annular space surrounding a heated inside tube of 17" length and ½" diameter positioned within an outside tube of ¾"

inside diameter. The inside tube is heated by means of a heating coil positioned therein to a temperature of either 300° or 400° F. depending upon the particular fuel being evaluated. The test is conducted for 300 minutes, at a pressure of 160 pounds per square inch, and a flow rate of 6 pounds of fuel per hour. Following the run the equipment is dismantled, 13" or less of the inner tube is marked off in 1" increments and the deposits on the outside surface of the heated inner tube are rated by visual comparison with standard metal coupons. In general the rating is substantially as follows:

- 0—clean and bright
- 1—metal dulled but not discolored
- 2—light yellow discoloration
- 3—yellow to tan discoloration
- 4—anything darker or heavier than 3

The ratings for the individual 1" increments are added together to give a final tube rating. Military specifications for jet fuels require that none of the 1" increments rates poorer than 3.

In this example, the jet fuel was evaluated at 400° F. A sample of the fuel without additive had a tube rating of 28. Another sample of the fuel containing 0.005% by weight of the ester of this example had a fuel rating of 18. As hereinbefore set forth, this is an exceptionally good result in view of the fact that a number of other additives were of substantially no benefit when run in this jet fuel.

EXAMPLE V

The ester of this example was prepared using a mixed acid available commercially as "Aliphath 44-A" and is derived from tall oil. This is a mixture of about 47% oleic acid and about 47% linoleic acid.

209 grams of a condensation product (50% solution in xylene) prepared in the manner described in Example I was commingled with 96.3 grams of the mixed acid. The condensation product was used in a concentration of ½ equivalent based on hydroxyl content and the mixed acid was used in a concentration of ½ mol. The mixture was boiled under refluxing conditions for 9 hours, during which time a total of 10.2 cc. of water was collected. The xylene was removed by distilling at 175° C. under water pump vacuum. The ester was recovered as a solid gel.

The ester prepared in the above manner also was evaluated by the fuel coker thermal stability test described in Example IV in another sample of the J.P.-6 jet fuel also described in that example.

0.005% by weight of the ester of this example was incorporated in another sample of the jet fuel and, when evaluated in the above manner, had a fuel rating of 19. This is to be compared with the fuel rating of 28 obtained in the absence of the additive. As mentioned in Example IV, this result is exceptionally good in view of the difficulty in benefiting this particular jet fuel with an additive.

EXAMPLE VI

The ester of this example was prepared using a mixed tall oil derived acid available commercially as "Crofatol #1" and contains about 51% oleic acid and about 46% linoleic acid. This ester was prepared in substantially the same manner as described in Example V. The ester was recovered as a viscous dark brown liquid and had an index of refraction n_D^{20} of 1.4807.

The ester prepared in the above manner was evaluated as a pour point depressant in lubricating oil. The lubricating oil was a commercial S.A.E. 20 Mid-Continent solvent extracted oil which, without additive, had an ASTM cold test of 5° F. and an ASTM pour point of 10° F. 1% by weight of the ester prepared in the above manner was incorporated in a sample of this lubricating oil and served to reduce the ASTM cold test to -10° F. and the ASTM pour point to -5° F. It will be noted that this additive was effective as a pour point depressant.

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EXAMPLE VII

An ester prepared in substantially the same manner as described in Example III was evaluated as a lubricating oil additive and tested in a Lauson engine operated at high oil temperature (280° F.) and low jacket temperature (210° F.). A typical commercial paraffinic solvent-extracted lubricating oil was used.

1% by weight of the ester was incorporated in the lubricating oil. In addition, 0.5% by weight of a diaminodiphenyl ether antioxidant also was incorporated in the oil. For comparison purposes, the following table reports the results when using a sample of the oil without additive and also another sample of the oil containing only the diaminodiphenyl ether antioxidant.

Table I

Run Number.....	1	2	3
Additive.....	None	Diaminodiphenyl ether antioxidant	Ester plus diaminodiphenyl ether antioxidant
Piston rating ¹	7	2.5	7.
Oil ring plugging, percent.....	5	10	0.
Sludge: ¹			
In crank case.....	10	10	10.
In sump.....	10	3	10.
Bearing weight loss, gms.....	2.9021	0.0117	0.1559.
Oil consumption.....	6.03	4.9	5.22.
Used Oil:			
Neutralization No.....	10.78	0.22	0.093.
Pentane Insoluble.....	5.16	0.22	0.21.
Viscosity at 100° F.....	742	364	399.
Viscosity at 210° F.....	74.7	54.2	56.1.

¹ CRC photos as guide, 10=clean, 0=dirty.

From the data in the above table, it will be noted that the additive of the present invention considerably improved the lubricating oil. The high piston rating was maintained in spite of the considerable drop when using the diaminodiphenyl ether antioxidant alone. The ring plugging was reduced to zero. The sludge in the crank case was clean, in contrast to the dirty crank case obtained when using the diaminodiphenyl ether antioxidant alone. The bearing weight loss, oil consumption and used oil neutralization number were all considerably improved. It is particularly notable that the pentane insoluble and viscosity of the used oil was considerably improved as compared to the oil without additive.

EXAMPLE VIII

The ester of this example is a caprylic acid ester of a condensation product (50% solution in xylene) prepared in substantially the same manner as described in Example I. As hereinbefore set forth, economic advantages accrue to the use of mixed acids available commercially. Accordingly, the caprylic acid used in this example is available commercially as "Neo-Fat 8" and comprises 93% caprylic acid, 4% capric acid and 3% caproic acid. 224.7 grams of the 50% active ingredient solution in xylene of the condensation product was commingled with 48.7 grams of the mixed acid. The condensation product was used in a concentration equivalent to 1/3 of the hydroxyl content and the acid was used in a concentration of 1/3 mol. The mixture was refluxed for 16 hours and a total of 11.4 cc. of water was collected. The xylene was removed by distilling at 155° C. under water pump vacuum. The ester was recovered as a viscous brown oil having an index of refraction n_D^{20} of 1.4702. It was readily soluble in a concentration of 50% in lubricating oil.

EXAMPLE IX

The ester of this example is a capric ester of a condensation product prepared in substantially the same manner as described in Example I. Here again a commercially available mixed acid was used. This acid is avail-

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able commercially as "Neo-Fat 10" and comprises 92% capric acid, 5% lauric acid and 3% caprylic acid. This ester was prepared substantially in the same manner as described in Example VIII. A total of 11.3 cc. of water was collected. The product is a dark brown gel which becomes fluid when heated to 80° F. or higher. The ester had an index of refraction n_D^{20} of 1.4704.

EXAMPLE X

The ester of this example is a coco ester of a condensation product prepared as described in Example I. The mixed acid used in this preparation is available commercially as "Neo-Fat 255" and contains 57% lauric acid, 21% myristic acid, 10% palmitic acid, 7% oleic acid, 3% linoleic acid and 2% stearic acid. 224.7 grams of the condensation product (50% solution in xylene) were refluxed with 69.5 grams of the coco acid for 16 hours, and the xylene later removed by distilling at 150° C. under water pump vacuum. The product was recovered as an amber colored waxy solid which was soluble in lubricating oil up to 50% by weight concentration.

EXAMPLE XI

The ester of this example is an isodecanoic acid ester of a condensation product prepared in the manner described in Example I. 326 grams of the condensation product (50% solution in xylene) were mixed with 79.5 grams of the isodecanoic acid and the mixture was refluxed for 16 hours. The ester was recovered as a free flowing dark brown oil having an index of refraction n_D^{20} of 1.4710.

EXAMPLE XII

The ester of this example is a naphthenic acid ester of a condensation product prepared as described in Example I. The naphthenic acid is a commercially available mixture. 209.6 grams of the condensation product (50% solution in xylene) were refluxed with 75.8 grams of the naphthenic acid for 16 hours. A total of 10 cc. of water was collected. The xylene was removed by distillation at 195° C. under water pump vacuum. The ester was recovered as a dark brown viscous liquid which was soluble in a concentration of 50% by weight in lubricating oil.

EXAMPLE XIII

The ester of this example is an oleic acid ester of a condensation product prepared as described in Example I. 200 grams of the condensation product (50% solution in xylene), 83.4 grams of oleic acid and 190 cc. of xylene were refluxed in a Dean-Stark water trap. 4.5 cc. of water was recovered. The resultant mixture was blended with additional xylene to a total weight of 358.6 grams, thereby giving a 50% by weight active ingredient solution.

As hereinbefore set forth, the additive of the present invention serves to permit hydrocarbon oils to pass the water tolerance test. According to this test as specified in MIL-I-25017, 20 ml. of a buffered or distilled water is placed in a 100 ml. glass stoppered graduated cylinder, and 80 ml. of isooctane containing the additive is commingled with the water. The cylinder is shaken for 2 minutes and allowed to stand undisturbed for 5 minutes. The interface then is inspected for any signs of emulsion, scum or foreign matter.

The ester prepared in this example was added in a concentration of greater than 200 parts per million to the isooctane and, when evaluated in the water tolerance test described above, satisfactorily passed this test. Because the additives used in oils which are subjected to this test are not used in concentrations greater than 200 parts per million, it was unnecessary to evaluate the ester in higher concentrations. However, as mentioned above, the oil containing the ester in a concentration of 200 parts per million readily passed this test.

EXAMPLE XIV

The ester of this example is a Petrex acid ester of a condensation product prepared as described in Example I. As hereinbefore set forth, Petrex acid is primarily a dibasic acid having an acid number of approximately 530 and a molecular weight of 215. Here again, this is a mixed acid available commercially at lower cost and accordingly advantageously is used in the present invention. 400 grams of the condensation product (50% solution in xylene), 62 grams of Petrex acid (equivalent weight of 104) and 110 cc. of xylene were refluxed overnight. 4 cc. of water was recovered. The resultant mixture was blended with xylene to a total weight of 524 grams, thereby giving a final solution of 50% by weight of active ingredient.

The ester prepared in the above manner was evaluated according to a test used to rate diesel fuels and fuel oils. In this test 50 cc. of the oil to be tested is placed in a 150 ml. beaker and then heated to 300° F. for 90 minutes. The beaker is allowed to cool to room temperature and the contents are filtered through filter paper. The paper then is dried and used for rating the fuel. In order to pass this test, the fuel containing the additive must give no more increase in color on the paper than is obtained by carrying out the test with a standard sample of the fuel. The discoloration then is evaluated by determining the reflectance.

The diesel oil used in this test is a blend of 30% range oil and 70% catalytic cycle stock. A control sample of the fuel, before heating, gave a reflectance reading of 97 which, however, after heating as described above, rated only 29. 80 parts per million of the ester prepared as described above and 5 parts per million of a commercial copper deactivator were incorporated in another sample of this fuel. When evaluated in this test, the oil containing the additives gave a reflectance reading of 84. The copper deactivator was added in a small concentration in order to simulate commercial practice which is to also add a copper deactivator to the fuel. From the above data, it will be seen that the ester of the present invention was effective in permitting the oil to pass the diesel oil stability test.

I claim as my invention:

1. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of a carboxylic acid of from about 6 to about 50 carbon atoms per molecule and the condensation product of from 1 to 2 mols of an epihalohydrin compound with from 1 to 2 mols of an aliphatic amine having from about 12 to about 40 carbon atoms per molecule, said epihalohydrin compound being selected from the group consisting of epichlorohydrin, 1,2-epi-4-chlorobutane, 2,3-epi-4-chlorobutane, 1,2-epi-5-chloropentane, 2,3-epi-5-chloropentane and corresponding bromo and iodo compounds, the amount of said acid being sufficient to esterify from one to all of the hydroxyl groups in said condensation product.

2. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of stoichiometric amounts of a monobasic carboxylic acid containing from about 6 to about 25 carbon atoms per molecule and the condensation product of from 1 to 2 mols of epichlorohydrin with from 1 to 2 mols of an alkyl amine having from about 12 to about 40 carbon atoms per molecule.

3. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of stoichiometric amounts of a dibasic carboxylic acid containing from about 6 to about 50 carbon atoms per molecule and the condensation product of from 1 to 2 mols of epichlorohydrin with from 1 to 2 mols of an alkyl amine having from about 12 to about 40 carbon atoms per molecule.

4. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of stoichiometric amounts of a naphthenic acid and the condensation product of

from 1 to 2 mols of epichlorohydrin with from 1 to 2 mols of an alkyl amine having from about 12 to about 40 carbon atoms per molecule.

5. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an oleic acid ester of the condensation product of equimolar amounts of epichlorohydrin and tallow amine, the ester being formed from one mol equivalent of acid per each equivalent of hydroxyl group in the condensation product.

6. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of a stearic acid ester of the condensation product of equimolar amounts of epichlorohydrin and tallow amine, the ester being formed from one mol equivalent of acid per each equivalent of hydroxyl group in the condensation product.

7. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of a 2-ethylhexoic acid ester of the condensation product of equimolar amounts of epichlorohydrin and tallow amine, the ester being formed from one mol equivalent of acid per each equivalent of hydroxyl group in the condensation product.

8. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of stoichiometric amounts of a terpene-maleic anhydride reaction product and the condensation product of equimolar amounts of epichlorohydrin and tallow amine.

9. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of a naphthenic acid and the condensation product of from 1 to 2 mols of epichlorohydrin with from 1 to 2 mols of tallow amine, the ester being formed from one mol equivalent of acid per each equivalent of hydroxyl group in the condensation product.

10. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of a carboxylic acid of from about 6 to about 50 carbon atoms per molecule and the condensation product, formed at a temperature from about 20° C. to about 150° C., of from 1 to 2 mols of an aliphatic amine containing from about 12 to about 40 carbon atoms per molecule with from 1 to 2 mols of an epihalohydrin compound selected from the group consisting of epichlorohydrin, 1,2-epi-4-chlorobutane, 2,3-epi-4-chlorobutane, 1,2-epi-5-chloropentane, 2,3-epi-5-chloropentane and corresponding bromo and iodo compounds, the amount of said acid being sufficient to esterify from one to all of the hydroxyl groups in said condensation product.

11. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of stoichiometric amounts of a carboxylic acid of from about 6 to about 50 carbon atoms per molecule and the condensation product, formed at a temperature of from about 20° C. to about 150° C., of equimolar amounts of epichlorohydrin and an alkyl amine of from about 12 to about 40 carbon atoms per molecule.

12. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an ester of a carboxylic acid of from about 6 to about 50 carbon atoms per molecule and the condensation product, formed at a temperature of from about 20° C. to about 150° C., of equimolar amounts of epichlorohydrin and tallow amine, the ester being formed from one mol equivalent of acid per each equivalent of hydroxyl group in the condensation product.

13. The hydrocarbon oil composition of claim 12 further characterized in that said acid is a fatty acid.

14. The hydrocarbon oil composition of claim 12 further characterized in that said acid is a naphthenic acid.

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