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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, resulting in decreased efficiency of 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 hot lubricating oil. 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 kerosene, diesel oil, heater oil, burner oil, range oil, gas oil, fuel oil, transformer oil, hydraulic oil, slushing oil, residual oil, 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 or sediment formation in storage tanks. 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 oil, gas turbine oil, steam turbine oil, jet turbine oil, marine oil, 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 separation of layers in order for the oil to pass this test. As will be shown in the appended examples, the additive of the present invention offers the additional advantage of not interfering with the hydrocarbon oil passing this test as some other additives will do.

In one embodiment the present invention relates to a method of improving a hydrocarbon oil which comprises incorporating therein a stabilizing concentration of an alkyl acid phosphate salt of an ester of a carboxylic acid and the condensation product of an epihalohydrin compound with an amine compound.

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, mixed mono- and ditridecyl acid orthophosphate salts of an ester formed from stearic 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 jet fuel which comprises incorporating therein a stabilizing concentration of mixed mono- and diisooctyl acid orthophosphate salts of an oleic acid ester of the condensation product of epichlorohydrin with 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 alkyl acid phosphate salt of an ester formed from a carboxylic acid and the condensation product of an epihalohydrin compound with an amine compound. The condensation products of epihalohydrin compounds with amines are very effective additives for hydrocarbon oils. However, with certain oils and for some purposes, carboxylic acid esters of the condensation products offer advantages. Similarly, with certain oils and for some purposes the alkyl acid phosphate salts of the esters offer advantages, and these novel additives are being disclosed and claimed in the present application.

### Condensation product of epihalohydrin with amine

The condensation product of epihalohydrin compound with amine compound is prepared in the manner described below. Any suitable amine compound may be used in preparing the condensation product and in one embodiment preferably contains at least 12 carbon atoms and still more 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 still more 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 may be used in preparing the condensation product. 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. 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 16 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-amyldodecyl amine, N-butyl-tridecyl amine, N-amyiltridecyl 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 is "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, etc. As before, mixtures are available commercially, usually at lower prices, of suitable 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, usually are not preferred. Illustrative examples of such compounds include 1,12-diaminododecane, 1,13-diaminotridecane, 1,14-diaminotetradecane, etc.

In general the preferred amine compounds are saturated; i.e., do 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 polybutylene polyamines, etc.

As hereinbefore set forth, the amine compound is reacted with an epihalohydrin compound. Epichlorohydrin is preferred. Other epichlorohydrin compounds include

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1,2-epi-4-chlorobutane, 2,3-epi-4-chlorobutane, 1,2-epi-5-chloropentane, 2,3-epi-5-chloropentane, etc. In general, the chloro derivatives are preferred, although it is understood that the corresponding bromo and iodo compounds may be employed. In some cases epidiolohydrin compounds may be utilized. It is understood that the different epihalohydrin compounds are not necessarily equivalent and that, as hereinbefore set forth, epichlorohydrin is preferred.

In general, 1 or 2 mols of amine compound are reacted with 1 or 2 mols of epihalohydrin compound. It is understood that, in some cases, an excess of amine or of epihalohydrin may be supplied to the reaction zone in order to insure complete reaction, the excess being removed subsequently in any suitable manner. When 2 mols of amine are reacted per mol of epihalohydrin compound, the amine may comprise the same or different amine compound.

In a preferred embodiment, the reaction of 1 mol of amine compound with 1 mol of epihalohydrin compound proceeds to the formation of polymeric reaction product. In this embodiment, the reaction is first effected at a temperature within the range hereinafter set forth, with only a portion of the reactants being present in the reaction mixture. After the initial reaction is completed, the remaining reactants are supplied to the reaction mixture and the reaction is completed at a higher temperature but within the same range set forth herein. For example, a portion of the amine may be first reacted with the epihalohydrin and then the remaining portion of the amine is reacted. These polymers may contain from about 3 to about 20 or more recurring units and preferably from about 5 to about 10 recurring units.

The desired quantity of alkyl amine and epihalohydrin compounds may be supplied to the reaction zone and therein reacted, although generally it is preferred to supply one reactant to the reaction zone and then introduce the other reactant stepwise. Thus, usually it is preferred to supply the amine to the reaction zone and to add the epihalohydrin compound step-wise, with stirring. When it is desired to react two different alkyl amines with the epihalohydrin compound, the epihalohydrin compound is supplied to the reaction zone. One of the amines is added gradually, and the reaction completed, followed by the addition of the second alkyl amine. Generally, it is preferred to utilize a solvent and, in the preferred embodiment, a solution of the amine in a solvent and a separate solution of the epihalohydrin compound in a solvent are prepared, and these solutions then are commingled in the manner hereinbefore set forth. Any suitable solvent may be employed, a particularly suitable solvent comprising an alcohol including ethanol, propanol, butanol, etc., 2-propanol being particularly desirable.

The reaction is effected at any suitable temperature, which generally will be within the range of from about 20° to about 100° C. and preferably is within the range of from about 50° to about 75° C. A higher temperature range of from about 30° to about 150° C. or more, and preferably of from about 50° to about 100° C., is specified when the reaction is effected at superatmospheric pressure to increase the reaction velocity. Conveniently, this reaction is effected by heating the amine solution at refluxing conditions, with stirring, gradually adding the epihalohydrin compound thereto, and continuing the heating until the reaction is completed.

Either before or after removal of the reaction product from the reaction zone, the product is treated to remove halogen, generally in the form of an inorganic halide salt as, for example, the sodium halide salt. This may be effected in any suitable manner and generally is accomplished by reacting the product with a strong inorganic base such as sodium hydroxide, potassium hydroxide, etc., to form the corresponding metal halide. The reaction to form the metal halide generally is effected under the same conditions as hereinbefore set forth. After this reaction

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is completed, the metal halide is removed in any suitable manner, including filtration, centrifugal separation, etc. It is understood that the reaction product also is heated sufficiently to remove alcohol and water and this may be effected either before or after the treatment to remove the inorganic halide.

In still another embodiment, after the reaction product of an alkyl amine and epihalohydrin is prepared, the reaction product may be reacted with other nitrogen-containing compounds including, for example, alkanol amines, urea, etc., instead of with the same or different alkyl amine as hereinbefore described. Illustrative alkanol amines include ethanol amine, propanol amine, butanol amine, pentanol amine, hexanol amine, etc.

#### Esters of the condensation product

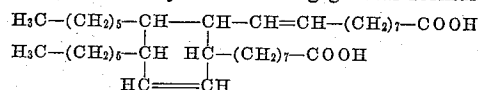
In the next step, an ester of a carboxylic acid and the condensation product described above is prepared. Any suitable carboxylic acid may be used in forming the ester and in one embodiment preferably comprises a monobasic carboxylic acid containing at least 6 carbon atoms, more particularly from 6 to about 25 carbon atoms, and thus includes caproic, caprylic, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, cerotic, etc., decylenic, dodecylenic, palmitoleic, oleic, ricinoleic, petroselinic, vaccenic, linoleic, linolenic, eleostearic, licanic, parinaric, gadoleic, arachidonic, cetoleic, erucic, selacholeic, etc.

However, in some cases, lower monobasic carboxylic acids may be employed and thus include formic, acetic, propionic, butyric, valeric, trimethylacetic, etc.

In another embodiment a polycarboxylic acid is used in forming the ester and preferably comprises a dibasic carboxylic acid containing at least 6 and preferably at least 10 carbon atoms per molecule, and more particularly from about 20 to about 50 carbon atoms per molecule. The preferred acids are referred to herein as high molecular weight polybasic carboxylic acids and include adipic, pimelic, suberic, azelaic, sebacic, phthalic, etc., aconitic, citric, etc., hemimellitic, trimelic, prehnitic, mellophanic, pyromellitic, mellitic, etc., and higher molecular polybasic carboxylic acids. It is understood that a mixture of acids may be employed.

A particularly preferred acid comprises a mixed by-product acid being marketed commercially under the trade name of "VR-1 Acid." This acid is a mixture of polybasic acids, predominantly dibasic, has an average molecular weight by basic titration of about 750, an average molecular weight of about 1000, is a liquid at 77° F., has an acid number of about 150 and iodine of about 37, and contains about 37 carbon atoms per molecule.

Another particularly preferred acid comprises a mixed acid being marketed commercially under the trade name of "Empol 1022." This dimer acid is a dilinoleic acid and is represented by the following general formula:



This acid is a viscous liquid, having an apparent molecular weight of approximately 600. It has an acid value of 180-192, an iodine value of 80-95, a saponification value of 185-195, a neutralization equivalent of 290-310, a refractive index at 25° C. of 1.4919, a specific gravity at 15.5° C./15.5° C. of 0.95, a flash point of 530° F., a fire point of 600° F., and a viscosity at 100° C. of 100 centistokes.

As hereinbefore set forth, dibasic acids containing at 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, maleic, 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, l-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 such 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, etc. 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.

In preparing the ester of the condensation product, the aliphatic carboxylic acids generally are preferred as hereinbefore set forth. However, 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, camphononic 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 alcohol portion of the ester but preferably contain 1 or 2 carbon atoms. The alcohol 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 alcohol group is volatilized off and replaced by 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 of 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 110° C., and with xylene in the order of 140-145° 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.

#### *Alkyl acid phosphate salts of the esters*

In the next step, the alkyl acid phosphate salts of the esters described above are prepared. The term "alkyl acid phosphate" includes both the alkyl acid orthophosphates and the alkyl acid pyrophosphates. In the alkyl acid orthophosphates, the monoalkyl ester, dialkyl ester or a mixture thereof may be employed. In the alkyl acid pyrophosphates, the monoalkyl ester, dialkyl ester, trialkyl ester or mixtures thereof may be employed, the dialkyl ester being preferred and the alkoxy groups may be attached to the same or different phosphorus atoms. Generally, however, this compound will be symmetrical and, thus, the alkoxy groups will be attached to different phosphorus atoms.

In general, at least one of the alkyl groups constituting the ester contains at least 5 and preferably at least 8 carbon atoms. Illustrative alkyl acid orthophosphates are set forth below, although it is understood that these are presented as preferred examples and that other suitable alkyl acid phosphates may be employed. The preferred alkyl acid orthophosphates include monoamyl acid orthophosphate, diamyl acid orthophosphate, mixture of mono- and diamyl acid orthophosphates, monohexyl acid orthophosphate, dihexyl acid orthophosphate, mixture of mono- and dihexyl acid orthophosphates, monoheptyl acid orthophosphate, diheptyl acid orthophosphate, mixture of mono- and diheptyl acid orthophosphates, mono-

octyl acid orthophosphate, dioctyl acid orthophosphate, mixture of mono- and dioctyl acid orthophosphates, monononyl acid orthophosphate, dinonyl acid orthophosphate, mixture of mono- and dinonyl acid orthophosphates, monodecyl acid orthophosphate, didecyl acid orthophosphate, mixture of mono- and didecyl acid orthophosphates, monoundecyl acid orthophosphate, diundecyl acid orthophosphate, mixture of mono- and diundecyl acid orthophosphates, monododecyl acid orthophosphate, didodecyl acid orthophosphate, mixture of mono- and didodecyl acid orthophosphates, monotridecyl acid orthophosphate, ditridecyl acid orthophosphate, mixture of mono- and ditridecyl acid orthophosphates, monotetradecyl acid orthophosphate, ditetradecyl acid orthophosphate, mixture of mono- and ditetradecyl acid orthophosphates, monopentadecyl acid orthophosphate, dipentadecyl acid orthophosphate, mixture of mono- and dipentadecyl acid orthophosphates, etc.

Preferred alkyl acid pyrophosphates include mono-octyl acid pyrophosphate, dioctyl acid pyrophosphate, mixture of mono- and dioctyl acid pyrophosphates, monononyl acid pyrophosphate, dinonyl acid pyrophosphate, mixture of mono- and dinonyl acid pyrophosphates, monodecyl acid pyrophosphates, didecyl acid pyrophosphate, mixture of mono- and didecyl acid pyrophosphates, monoundecyl acid pyrophosphate, diundecyl acid pyrophosphate, mixture of mono- and diundecyl acid pyrophosphates, monododecyl acid pyrophosphate, didodecyl acid pyrophosphate, mixture of mono- and didodecyl acid pyrophosphates, monotridecyl acid pyrophosphate, ditridecyl acid pyrophosphate, mixture of mono- and ditridecyl acid pyrophosphates, monotetradecyl acid pyrophosphate, ditetradecyl acid pyrophosphate, mixture of mono- and ditetradecyl acid pyrophosphates, monopentadecyl acid pyrophosphate, dipentadecyl acid pyrophosphate, mixture of mono- and dipentadecyl acid pyrophosphates, etc.

Conveniently, alkyl groups containing more than 8 carbon atoms are introduced through the use of fatty alcohols and thus the alkyl radical may be selected from capryl, lauryl, myristyl, palmityl, stearyl, ceryl, etc. Illustrative phosphates in this class include stearyl capryl acid orthophosphate, distearyl acid orthophosphate, dicapryl acid orthophosphate, etc. In other examples, one of the alkyl groups contains less than 8 carbon atoms while the second alkyl group contains more than 8 carbon atoms, and such examples are illustrated by ethyl lauryl acid orthophosphate, ethyl stearyl acid orthophosphate, hexyl lauryl acid orthophosphate, hexyl capryl acid orthophosphate, hexyl stearyl acid orthophosphate, etc.

Alkyl acid phosphates including both the ortho and pyrophosphates also are manufactured commercially as a mixture of mono- and dialkyl acid phosphates and are available at lower costs. In many cases, such mixtures are suitable for use in preparing the salt of the present invention and such use, therefore, is preferred for economic reasons.

The alkyl acid phosphate salt of the ester is prepared utilizing at least one mol of alkyl acid phosphate per mol of the ester and will range up to one mol of phosphate per each mol equivalent of basic nitrogen in the ester. In general this will comprise from about 2 to about 20 mols of phosphate per 1 mole of ester. For example, as hereinbefore set forth, the ester prepared from the polymer formed by the reaction of 1 mol of epichlorohydrin with 1 mol of amine compound will contain from about 3 to about 20 and preferably from about 5 to about 10 recurring units, each unit containing a basic nitrogen. Accordingly, from about 3 to about 20 mols of phosphate are used per mol of ester in order to obtain the desired salt. It is understood that, when the ester contains more than 20 basic nitrogens, a correspondingly larger amount of phosphate preferably is used. Thus, in a preferred salt of the present invention, an equivalent mol of phosphate is used per mol of basic

nitrogen, although in some cases, an excess of deficiency of phosphate may be used.

The salt may be prepared in any suitable manner and, in general, is prepared by admixing the alkyl acid phosphate and the ester at ambient temperature, preferably with vigorous stirring. The salt is readily prepared at room temperature, although slightly elevated temperatures which generally will not exceed 200° F. may be employed, when desired. Excessive temperatures must not be used in order to avoid decomposition reactions. In fact, the reaction is slightly exothermic and in some cases it may be desirable to cool the reaction vessel. The reaction may be effected in the presence or absence of a solvent. When employed, the solvent may be used either in forming a more fluid mixture of the reactants before mixing and/or used during the mixing thereof. Any suitable solvent may be employed and preferably is an aromatic hydrocarbon including benzene, toluene, xylene, ethylbenzene, cumene, etc., or mixtures thereof. In other cases the solvent may be selected from alcohols, ethers, ketones, etc. In many cases it is desired to market the salt as a solution in a suitable solvent and conveniently the same solvent is used during manufacture of the salt as desired in the final product.

The concentration of salt to be incorporated in the hydrocarbon oil will depend upon the particular use. For example, when utilized to prevent heat exchanger deposits, the salt generally is used in a concentration of from 1 to 1000 parts and preferably from 10 to 200 parts per million by weight of the hydrocarbon oil. When used for other purposes, the salt is 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 salt 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 salt 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, alumina-molybdenum sulfide-cobalt sulfide or other suitable catalysts. 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 to 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 exchanger 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 the 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 salt 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 incorporated in the oil for specific reasons as, for example, metal deactivator, antioxidant, synergist, cetane improver, etc. As hereinbefore set forth, the salt 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 salt of this example is the mixed mono- and ditridecyl acid orthophosphate salts of the adipic acid ester of the condensation product of epichlorohydrin with 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.

100 grams of the 50% solution of the condensation product prepared in the above manner were mixed with 21 grams of adipic acid and 55 cc. of xylene. The mixture was refluxed at a temperature of about 142° C. for about 7 hours. A total of 2.5 cc. of water was collected. Additional xylene was added to produce a final solution of 50% by weight active ingredient.

20 grams of the 50% active ingredient solution of the ester prepared in the above manner were commingled with 8 grams of mixed mono- and ditridecyl acid ortho-

phosphates along with 10 cc. of xylene. The mixture was heated slowly to 50° C. and allowed to react for approximately 50 minutes. The product was cooled and blended with additional xylene to produce a final salt solution of 50% by weight active ingredient. The resulting solution was a dark amber, viscous liquid, having an index of refraction ( $n_D^{20}$ ) of 1.4862, a density ( $d_4^{20}$ ) of 0.9261. For identification purposes, the 50% active solution was subjected to vacuum distillation to remove the xylene solvent and to recover the active ingredient as a dark amber semi-solid which becomes a free flowing liquid at about 50° C. and which has a refractive index ( $n_D^{20}$ ) of 1.4771.

The salt 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 differential pressure across the filter of 25 in. Hg is determined. It is apparent that the longer the time, the more effective is the additive. However, with a vary effective additive, the time to reach a differential pressure across the filter of 25 in. Hg is lengthened beyond reasonable limits that the test is stopped after about 300 minutes and the differential pressure at that time is reported.

The oil used in this example is a commercial J.P.-6 jet fuel blend. When evaluated for use as a jet fuel, which normally encounters higher temperature, the test is run at higher temperature. In this particular test the preheater was run at the higher temperature of 450° F. and the filter at the higher temperature of 550° F.

When evaluated in the above manner, a sample of the jet fuel blend, without additive, developed a differential pressure across the filter of 25 in. Hg in 112 minutes. Another sample of this fuel containing 0.0005% by weight of the 50% active solution (accordingly only 0.00025% by weight of the active ingredient) developed a differential pressure of only 0.2 in. Hg after 300 minutes.

From the above data, it will be noted that the salt of the present invention was very effective in preventing filter plugging, even when evaluated at the higher temperature. Accordingly, the fuel containing the additive is satisfactory for use as a jet fuel, whereas plugging difficulties are encountered in the absence of the additive.

*Example II.*—The salt of this example is the monoisooctyl acid orthophosphate salt of the oleic acid ester of a condensation product prepared in substantially the same manner as described in Example I.

200 grams of the 50% active solution of the condensation product prepared in the manner described in Example I, 83.4 grams of oleic acid and 100 cc. of xylene were mixed and refluxed at about 147° C. for 20 hours, during which time a total of 4.5 cc. of water was collected.

20 grams of the ester solution prepared in the above manner, 4.94 grams of monoisooctyl acid orthophosphate and 5 cc. of xylene were mixed and heated, with stirring, gradually for one hour to bring the temperature up to 50° C. and then allowed to react for 30 minutes. The product was allowed to cool and then blended with 30 cc. of xylene to form a final solution of 50% by weight active ingredient. The solution had an index of refraction ( $n_D^{20}$ ) of 1.4834 and a density ( $d_4^{20}$ ) of 0.9007. For identification purposes, the solution was distilled under vacuum to remove the xylene and to leave a reddish brown viscous liquid having an index of refraction ( $n_D^{20}$ ) of 1.4717.

0.0005% by weight of the salt solution (0.00025% by weight active ingredient) prepared in the above manner was evaluated in the Erdco test in another sample of the jet fuel blend described in Example I and in the manner described therein. Here again, the evaluation was effected at the high preheater temperature of 450° F. and the high filter temperature of 550° F.

The sample of jet fuel blend containing the salt developed a differential pressure of only 0.4 in. Hg after 300 minutes. In contrast, a control sample (no additive) of the jet fuel blend developed a differential pressure of 25

in. Hg within 112 minutes. Here again it will be seen that the additive of the present invention was very effective in preventing filter plugging.

*Example III.*—The additive of this example is the mixed mono- and ditridecyl acid orthophosphate salts of the VR-1 acid ester of the condensation product prepared in the manner described in Example I. As hereinbefore set forth, VR-1 acid is a mixture of polybasic acids, predominantly dibasic, containing about 37 carbon atoms per molecule. The ester was prepared by admixing 100 grams of the condensation product prepared as described above, 101 grams of VR-1 acid and 120 cc. of xylene. The condensation product used in a concentration of hydroxyl equivalent of 0.148 and the VR-1 acid was used in a concentration of hydroxyl equivalent of 0.296. Because the VR-1 acid is predominantly dibasic, the hydroxyl groups which react are on an equivalent mol basis. The mixture was heated with stirring to a temperature of about 144° C. and refluxed for about 10 hours, during which time approximately 4 cc. of water were collected. The mixture was cooled and xylene was added to prepare a final solution of 50% by weight active ingredient.

30.1 grams of the ester prepared in the above manner, 5.27 grams of mixed mono- and ditridecyl acid orthophosphates and 6 cc. of xylene were mixed and heated, with stirring, to about 50° C. and allowed to react at this temperature for about 30 minutes. The product was cooled and blended with 40.5 cc. of xylene to prepare a final solution of 50% by weight active ingredient.

0.0005% by weight of the solution of salt described above (0.00025% by weight active ingredient) was incorporated in another sample of the jet fuel blend and evaluated in the Erdco test in the same manner as described in Example II. The jet fuel blend containing this additive developed a differential pressure of 0.1 in. Hg after 300 minutes. On the other hand, a sample of the jet fuel not containing the additive developed a differential pressure of 25 in. Hg within 112 minutes. Here again it will be seen that the additive of the present invention was very effective in retarding filter plugging.

*Example IV.*—The salt prepared as described in Example III also was evaluated in 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 salt prepared in this example was added in a concentration of 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 salt in higher concentrations. However, as mentioned above, the oil containing the salt in a concentration of 200 parts per million readily passed this test.

*Example V.*—The additive of this example is the mixed mono- and ditridecyl acid orthophosphate salts of the stearic acid ester of the condensation product prepared as described in Example I. The ester was prepared by mixing 200.2 grams of the condensation product prepared in the manner described in Example I, 79 grams of stearic acid and 100 cc. of xylene, and refluxing the mixture, with stirring, at a temperature of about 146° C. for about 10½ hours, during which time a total of 5 cc. of water was collected. The product was cooled to room temperature and blended with 348 grams of xylene to form a solution of 50% by weight active ingredient. The salt was prepared by commingling 30 grams of the ester prepared in the above manner, 9.5 grams of mixed mono- and ditridecyl acid orthophosphates and 10 cc.

of xylene. The mixture was stirred and heated gradually to a temperature of about 50° C. and then allowed to react at this temperature for about 35 minutes. The product was cooled and additional xylene was added to form a final solution of 50% by weight active ingredient. The solution had an index of refraction ( $n_D^{20}$ ) of 1.4817 and a density ( $d_4^{20}$ ) of 0.9010.

0.003% by weight of the salt solution prepared in the above manner (0.0015% by weight of active ingredient) was incorporated in a J.P.-6 jet fuel and evaluated in the Erdco test. This evaluation was made using a preheater temperature of 400° F. and a filter temperature of 500° F. A control sample (no additive) of this fuel developed a differential pressure of 25 in. Hg within 51 minutes. On the other hand, the sample of the jet fuel containing the salt did not develop any differential pressure after 300 minutes.

The mixed tridecyl salts of the stearic acid ester of the condensation product also were 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 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 15. Another sample of the fuel containing 0.003% by weight (0.0015% by weight of active ingredient) of the salt solution described above had a tube rating of 6 when evaluated in the above manner. Accordingly, it will be seen that the additive of the present invention reduced the tube rating to less than half of that obtained with the control sample (no additive) and thus reduces preheater deposits.

*Example VI.*—The additive of this example is the mixed mono- and ditridecyl acid orthophosphate salts of tall oil acid ester of the condensation product prepared as described in Example I. The tall oil acid comprises a mixture containing oleic, linoleic, linolenic and rosin acids. 200 grams of the condensation product, 85.5 grams of the tall oil acid and 90 cc. of xylene were commingled and heated with stirring at about 148° C. for about 9 hours, during which time 4 cc. of water were collected. After cooling, 363 cc. of xylene were added to prepare a solution containing 50% by weight of active ingredient.

20.1 grams of the ester prepared in the above manner, 6.2 grams of mixed mono- and ditridecyl acid orthophosphates were heated with stirring to 50° C. and allowed to react for about 1.5 hours. After cooling, the mixture was blended with xylene to produce a final solution containing 50% by weight active ingredient.

The salt prepared in the above manner was evaluated in the Erdco test using another sample of the jet fuel and in the same manner as described in Example V.

The additive was used in a concentration of 0.003% by weight (0.0015% active ingredient). After 300 minutes the sample of jet fuel containing the additive developed zero differential pressure. In contrast a sample of the jet fuel without additive developed a differential pressure of 25 in. Hg within 51 minutes.

*Example VII.*—The additive of this example is the mixed mono- and di-octyl acid orthophosphate salts of an oleic acid ester of the condensation product prepared according to the description in Example I. The acid used to prepare the ester is 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 advantage of the present invention that these mixed acids are used without the additional cost otherwise necessary to separate substantially pure acids.

209.6 grams of the condensation product (50% solution in xylene) prepared in the manner described in Example I were commingled with 94 grams of the mixed acid described above, and the mixture was refluxed with stirring, for about 10 hours, during which time 11.3 cc. of water were collected. Following completion of the reaction, the product was heated to 160°–170° C. under water pump vacuum to remove the xylene. The ester then was commingled, while stirring and warming, with mixed mono- and di-octyl acid orthophosphates in a concentration of phosphate equivalent to the basic nitrogen in the ester.

The salt prepared in the above manner was evaluated in the Erdco test using a J.P.-4 jet fuel which, without additive, developed a differential pressure of 25 in. Hg within 128 minutes. 0.00025% by weight of the salt prepared in the above manner was incorporated in another sample of the J.P.-4 fuel and, when evaluated in the same manner, developed a differential pressure of only 0.1 in. Hg in 300 minutes.

The salt prepared in the above manner also was evaluated as a pour point depressant in lubricating oil, which lubricating oil was an S.A.E. 20 Mid-Continent solvent extracted oil. This oil, without additive, had an ASTM cold test of 5° F. 1% by weight of the salt prepared in the above manner was incorporated in another sample of this lubricating oil and served to reduce the ASTM cold test to below –30° F.

*Example VIII.*—The additive of this sample is the mixed mono- and diisoamyl acid orthophosphate salts of the isodecanoic acid ester of a condensation product prepared as described in Example I. 169 grams of a condensation product prepared as described in Example I, 40 grams of isodecanoic acid and 100 grams of xylene were heated, with stirring, to refluxing temperature for 12 hours. A total of 12.2 cc. of water was collected. The mixture then was distilled under water pump vacuum to remove the xylene.

57.1 grams of the ester prepared in the above manner were mixed with 12.75 grams of mixed mono- and diisoamyl acid orthophosphates and warmed with stirring.

The salt prepared in the above manner was used as a pour point depressant in the lubricating oil described in Example VII. 1% by weight of the salt was incorporated in another sample of the lubricating oil and this served to reduce the ASTM cold test to –25° F. and the ASTM pour point to –20° F. This is in contrast to the corresponding numbers of 5° F. and 10° F., respectively, in the oil without the additive.

*Example IX.*—The salt of this example is the mixed mono- and diisoamyl acid orthophosphate salts of the tall oil acid ester of the condensation product prepared as described in Example I. The tall oil acid is available commercially as "Crofatol #1" and contains about 51% oleic acid and about 46% linoleic acid.

163.1 grams of the condensation product (50% solution in xylene) prepared as described in Example I, 70.7 grams of the mixed tall oil acid (Crofatol #1) and 100 grams of xylene were refluxed for about 13 hours. A

total of 4.8 cc. of water was collected. The product then was distilled at 150° C. under water pump vacuum to remove the xylene. 67.5 grams of the ester produced in the above manner were commingled with 12.75 grams of mixed mono- and diisoamyl acid orthophosphates with stirring and warming.

The salt prepared in the above manner was evaluated at a pour point depressant in lubricating oil. 1% by weight of the salt served to lower the ASTM cold test to –5° F. and the ASTM pour point to 0° F.

*Example X.*—The additive of this example is the mixed mono- and di-octyl acid orthophosphate salts of the naphthenic acid ester of the condensation product prepared in the manner 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 under water pump vacuum. The ester was recovered as a dark brown viscous liquid. The salt was prepared by mixing mono- and di-octyl acid orthophosphates with the naphthenic acid ester in an equivalent phosphate and basic nitrogen concentration and warming the mixture while stirring. The salt is incorporated in lubricating oil to serve to depress the pour point of the lubricating oil.

I claim as my invention:

1. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an alkyl acid phosphate salt 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 of 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 and the amount of alkyl acid phosphate being at least one mol of phosphate per mol of the ester.

2. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an alkyl acid phosphate salt of an ester of stoichiometric amounts of a 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, the amount of alkyl acid phosphate being from about 2 to about 20 mols of phosphate per mol of ester.

3. The hydrocarbon oil composition of claim 2 further characterized in that said alkyl acid phosphate is monoamyl acid orthophosphate.

4. The hydrocarbon oil composition of claim 2 further characterized in that said alkyl acid phosphate is mixed mono- and di-isoamyl acid orthophosphates.

5. The hydrocarbon oil composition of claim 2 further characterized in that said alkyl acid phosphate is mono-octyl acid orthophosphate.

6. The hydrocarbon oil composition of claim 2 further characterized in that said alkyl acid phosphate is mono- and di-octyl acid orthophosphates.

7. The hydrocarbon oil composition of claim 2 further characterized in that said alkyl acid phosphate is mixed mono- and ditridecyl acid orthophosphates.

8. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an alkyl acid phosphate salt 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 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 epihalo-

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hydrin 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 and the amount of alkyl acid phosphate being at least one mol of phosphate per mole of the ester.

9. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an alkyl acid phosphate salt 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, the amount of alkyl acid phosphate being from about 2 to about 20 mols of phosphate per mol of ester.

10. The hydrocarbon oil composition of claim 9 further characterized in that said phosphate is an alkyl acid orthophosphate.

11. The hydrocarbon oil composition of claim 9 further characterized in that said phosphate is an alkyl acid pyrophosphate.

12. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an alkyl acid orthophosphate

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salt 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 said condensation product and said salt being formed from an equivalent mol of phosphate per mol of basic nitrogen in the condensation product.

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