This invention relates to a novel method of preventing heat exchanger deposits.

In most refining operations economies are effected by utilizing the heat contained in hot products of the process to partially or completely heat the charge to the process or other low temperature streams. At the same time this serves to cool the hot products prior to further separation or treatment. This transfer of heat normally is accomplished by passing the hot products in indirect heat exchange with the cooler products. However, difficulty is experienced in the efficient transfer of heat due to the formation of deposits in the heat exchanger, which deposits interfere with the satisfactory transfer of heat and, in extreme cases, results in plugging of the heat exchanger. This in turn means that the unit must be completely shut down in order to clean or replace the heat exchanger. It is apparent that this is a serious problem and incurs great expense in shutting down the unit, both in the cost of cleaning or replacing the heat exchanger, as well as in the loss of products to be marketed. The present invention is directed to a novel method of preventing such heat exchanger deposits.

More particularly the present invention is directed to a modification of existing heat exchanging oil additives as will be set forth in detail hereinafter. These additives are effective for use in hydrocarbon oils to improve storage properties thereof, preventing sediment and sludge formation, discoloration and other undesirable deterioration of the hydrocarbon oil. However, hydrocarbon oils from different sources respond differently to different additives. Accordingly, the additives referred to above are effective for various purposes in some oils but are satisfactory for only limited purposes in other oils. For example, some of the additives satisfactorily stabilize the oil against deterioration in storage but will not satisfactorily prevent deposit formation in heat exchangers. As hereinbefore set forth, the novel additive of the present invention is particularly effective in preventing heat exchanger deposits and, at the same time, will serve to improve the storage stability of hydrocarbon oils.

In one 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 about 1 to about 1000 parts per million by weight of an oil soluble HCl salt of a compound selected from the group consisting of (1) the condensation product of an epihalohydrin compound with an amine compound, (2) carboxylic acid ester thereof, (3) partial phosphate salt of said condensation product, and (4) partial phosphate salt of said carboxylic acid ester thereof.

In a specific embodiment the present invention relates to a method of preventing deposit formation in a heat exchanger through which at least a portion of a hydrocarbon charge to a process is passed in heat exchange with a portion of hot reactor effluent products, which comprises incorporating in said charge from about 5 to about 20% of the amine nitrogen neutralized with HCl. As hereinbefore set forth, the novel additive of the present invention is an HCl salt of the condensation product of an epihalohydrin compound with an amine compound or derivatives thereof. The condensation product and the derivatives thereof will be described under subheadings to facilitate the expansion of the invention.

CONDENSATION PRODUCT OF EPIHALOHYDRIN WITH AMINE

Any suitable epihalohydrin compound may be utilized in preparing the condensation product thereof with an amine. Epichlorohydrin is preferred. Other epihalohydrin compounds include 1,2-epi-1-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 epihalohydrin 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.

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 atoms are substituted by alkyl groups, and reference to amine and amine compound in the present specifications and claims is intended to be limited accordingly. The preferred amine compounds are a primary amine which, in a specifically preferred embodiment, contains from about 12 to about 40 carbon atoms per molecule. Illustrative primary alkyl amines include dodecyl amine, tridecyl amine, tetradecyl amine, pentadecyl amine, hexadecyl amine, heptadecyl amine, octadecyl amine, nonadecyl amine, eicosyl amine, hendecyloxy amine, dodecyloxy amine, triclosyloxy amine, tetracosyloxy amine, pentacosyloxy amine, hexacosyloxy amine, heptacosyloxy amine, octacosyloxy amine, nonacosyloxy amine, triacontyl amine, hexatriacontyl amine, decacontyl amine, triacontyl amine, tetracontyl amine, pentacontyl amine, heptacontyl amine, octacontyl amine, nonacontyl amine, tetracontyl amine, tetacontyl amine, etc. Conven tional the long chain amines are prepared from fatty acids or more particularly from mixtures of fatty acids formed in the process of refining. 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 tall oil amine which is available under various trade names including "Alamine H26D" and "Alamine HTD." These products comprising 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. In most cases both of the alkyl groups have 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 lower price, and such mixtures may be used in accordance with the present
invention. An example of such a mixture available commercially is "Armeen 2HT" which consists primarily of dioctadecyl amine and dithexadecyl amine.

Preferred examples of N-alkyl polyamines comprise N-alkyl-1,3-diaminopropanes and still more preferably such compounds in which the alkyl group contains at least 2 carbon atoms. Illustrative examples include N - dodecyl - 1,3 - dianimopropane, 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 also contains a minor 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 in some cases. In other cases, polyamines may be employed as, for example, 1,12-diaminododecane, 1,13-diaminotridecane, etc.

In general the preferred amine compounds are saturated and do not contain double bonds in the chain. However, in some cases, unsaturated compounds may be employed, 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 dodecylecine amine, dodecylecine ethylene diamine, N-dodecylecine-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-linoele-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 epihalohydric compound. Both of the amines may be selected from those hereinbefore set forth or one of the amines is selected from those hereinbefore set forth and the other amine is selected from ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylen, pentamine, etc., similar propylene and polypropylene polyamines, butylene and polybutylene polyamines, etc.

In general, 1 or 2 mols of amine compound are reacted with 1 or 2 mols of epihalohydric compound. It is understood that, in some cases, an excess of amine or of epihalohydric 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 epihalohydric 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 epihalohydric 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 excess reactants are added 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 epihalohydric 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 epihalohydric 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 step-wise. Thus, usually it is preferred to supply the amine to the reaction zone and to add the epihalohydric compound step-wise, with stirring. When it is desired to react two different alkyl amines with the epihalohydric compound, the epihalohydric compound in a solvent are prepared, and these solutions are then condensed 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, usually in the epihalohydric 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 as, for example, the sodium halide. 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 the reaction 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 epihalohydric 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
Ester of the Condensation Product

As hereinbefore set forth, another embodiment of the present invention comprises an HCl salt of an ester of the condensation product of epibohydrin compound and amine compound. 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 caprylic, caprylic, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, cerotic, etc., dehydrogenated, palmitoleic, oleic, ricinoleic, petroselinic, vaccenic, linoleic, linolenic, eleostearic, liniceric, parinaric, gadoleic, arachidonic, erucic, erucicolenic, etc. However, in some cases, lower monobasic carboxylic acids may be employed and thus include formic, acetic, propanoic, butyric, valeric, threemethylvaleric, 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 polycarboxylic acids and include adipic, pimelic, suberic, azelaic, sebacic, phthalic, etc., acetic, citric, etc., hemimellitale, trimelic, prehnitic, melophanolic, pyromellitic, mellitic, etc., and higher molecular polycarboxylic acids. It is understood that a mixture of acids may be employed.

A particular 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 polycarboxylic acids, predominantly dibasic, has an average molecular weight about 750, is a liquid at 77°F, has an acid number of about 150 and iodine of about 36, and contains about 37 carbon atoms per molecule.

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

\[
\text{H}_2\text{C}-(\text{OH})_2-\text{OH}-\text{CH}-\text{CH}-(\text{OH})_2-\text{COOH} \\
\text{H}_2\text{C}-(\text{CH}_3)-\text{CH}_2-(\text{CH}_2)-\text{COOH} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O}
\]

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 of 1.093, a flash point of 350°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 terpene compound may be reacted with any suitable alpha, beta-unsaturated carboxylic acid or anhydride to form the product reaction of subsequent condensation with the epibohydrin-amine condensation product. In one embodiment a terpene hydrocarbon having the formula C₆H₆ is employed, including alpha-pinene, beta-pinene, dipentene, dl-limonene, l-limonene and terpinine. These terpenoiccarbons 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 alio-o-cymene, o-cymene, myrcene, etc. Other terpene 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 dibasic and carboxylic 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 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 of epibohydrin compound and amine compound, 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, toulene acid, etc., which acids also may contain hydrocarbon and particularly alkyl substituents attached to the ring. Naphthenic carboxylic acids include cyclopentane carboxylic acid; cyclopentenyl-acetic acid, methylocyclopentyl acetic acid, camphonic acid, cyclohexane carboxylic acid, methylcyclohexane carboxylic acid, dimethylcyclohexane carboxylic acid, trimethylcyclohexene 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 epibohydrin-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 epibohydrin-amine condensation product. In the esterification of the condensation product, transesterification occurs; that is, the smaller alcohol group is volatilzed off and replaced by the epibohydrin-amine condensation product.

The ester of the carboxylic acid and epibohydrin-amine condensation product may comprise the partially or completely esterified product. As hereinbefore set forth, the epibohydrin-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 the epalholhydrin-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 130°-140°C. Other preferred solvents include camphor, 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 hereinafter 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.

**PARTIAL PHOSPHATE SALTS OF THE CONDENSATION PRODUCT**

Another embodiment of the invention comprises an HCl salt of a partial phosphate salt of the condensation product of epalholhydrin compound and amine compound. As hereinafter set forth, the condensation product contains a number of recurring units, each unit containing a nitrogen atom. In this embodiment of the invention only a portion of the nitrogen atoms are neutralized with the phosphate, and all or a portion of the remaining nitrogen atoms are neutralized with HCl. Accordingly, this embodiment of the invention comprises the mixed HCl-phosphate salts of the condensation product.

In forming the phosphate salt, an alkyl acid phosphate preferably is utilized and may comprise the alkyl acid orthophosphate and/or the alkyl acid pyrophosphate. 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 alkyloxy groups may be attached to the same or different phosphorus atoms. Generally, however, this compound will be symmetrical and, thus, the alkyloxy groups will be attached to different phosphorus atoms.

Preferably at least one of the alkyloxy groups constituting the oxygen atoms contains at least 5 and still more 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 monomethyl acid orthophosphate, dimethyl acid orthophosphate, mixture of mono- and dimethyl acid orthophosphates, monohexyl acid orthophosphate, dihexyl acid orthophosphate, mixture of mono- and dihexyl acid orthophosphates, monododecyl acid orthophosphate, mixture of mono- and dodecyl acid orthophosphates, mixture of mono- and tetradecyl acid orthophosphates, mixture of mono- and capryl acid orthophosphates, etc.

8. Monophosphate salts of the condensation product.


11. Use of the partial phosphate salts.

12. Other embodiments of the invention.

13. Claims.

Neutralization with HCl is effected in any suitable manner and in general is readily accomplished by heating, with stirring, a mixture of the condensation product, ester or partial phosphate salt and HCl. The HCl may be utilized as a gas in a closed system. However, it preferably is utilized as a solution in a suitable solvent including alcohol, water, etc. The lower alcohols are preferred solvents and include methanol, ethanol, propanol, and butanol. In general the reaction is effected at ambient or elevated temperature, which may range from about 50° to about 100° C. and, as stated before, with stirring. Higher temperatures may be used in some cases, but generally offer no advantages. When a solvent is employed, it may be removed by distillation under vacuum or in any other suitable manner, although in some cases it may be desirable to market the additive as a solution in the solvent. When water is used as the solvent, the water preferably is removed by azeotropic distillation.

The HCl salt recovered in the above manner may be utilized as such or prepared as a solution in a suitable solvent. Aromatic hydrocarbons are particularly preferred solvents and include benzene, toluene, xylene, ethylbenzene, cumene, etc. It is understood that other suitable organic compounds and particularly paraffinic hydrocarbons may be used as solvents.

The additive prepared in the above manner is incorporated in a hydrocarbon oil in an amount of from about 1 to about 1000 parts per million by weight of the hydrocarbon oil and preferably in a concentration of from about 5 to about 100 parts per million, although higher concentrations up to 1% by weight may be used in some cases and thus may range from about 0.0005% to about 1% by weight.

As hereinafter set forth, the salt of the present invention is utilized to prevent deposit formation in heat exchangers. In such heat exchange one fluid is passed through tubes or coils disposed in a shell and the other fluid is passed through the shell. The oil heated in this manner then is passed for further treatment, while the oil cooled in this manner is passed to separation or further conversion. It is understood that the hydrocarbon oil may comprise gasoline, naphtha, kerosene, gas oil, burner oil, diesel oil, fuel oil, residual oil, etc.

An example of a process in which the charge is passed in heat exchange with hot effluent products is a hydrogen treating 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 may comprise gasoline, kerosene, gas oil or mixtures thereof and is treated to remove impurities including sulfur compounds, nitrogen compounds, oxygen compounds, metals, etc. The treating is effected at a temperature within the range of from about 500° to about 800° F. or more at hydrogen pressures of from about 100 to about 1000 pounds per square inch or more. The oil charged to the process generally is introduced at a temperature of from ambient to 200° F. and is passed in heat exchange with products withdrawn from the reactor at a temperature of from about 500° to about 800° F. During this heat exchange the charge is heated to a temperature of from about 300° to about 600° F. and then may be heated further in a furnace or otherwise to the temperature desired for effecting the treating. At the same time the hot reactor effluent products are cooled to a temperature of from about 300° to about 600° F. and below that at which they are withdrawn from the reactor. The partly cooled reactor effluent products are cooled further by heat exchange with water or otherwise and then are passed into a separator, wherefrom gases and liquids are each separately withdrawn. Another illustrative example of a process in which the charge is passed in heat exchange with reactor effluent 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. 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.

Normally the charge to the treating or conversion process contains components which form deposits in the heat exchangers and, accordingly, the salt of the present invention is incorporated in the charge prior to entering the heat exchanger. In most cases the charge after heat exchange is subjected to fractionation to separate a particular stream for subjecting to further treating or conversion in the presence of a catalyst. Generally this stream comprises the light or intermediate fractions of the charge, and the heavier components of the charge are removed from the process. In most cases the salt will be retained in the bottoms product and therefore will not contact the catalyst used in the subsequent treating or conversion steps. However, the salt in the small concentrations used will not adversely affect most catalysts, and therefore would be of concern only with processes using catalysts of extreme sensitivity. As stated above, even with such catalysts, the prefractionation will serve to retain the salt in the heavier products and the salt therefore will not contact the catalyst.

Another example in which hydrocarbon oil is passed in heat exchange is in the case of jet fuel, wherein the jet fuel is passed in heat exchange with hot lubricating oil. Temperatures as high as 300° F. or more are encountered for at least short periods of time, with the result that deposit formation occurs and either interferes with efficient heat transfer or, in extreme cases, plug the heat exchanger.

As hereinafore set forth, the additive of the present invention also may be used to improve the storage stability and other properties of hydrocarbon oil. These hydrocarbon oils include gasoline, naphtha, kerosene, gas oil, burner oil, diesel oil, fuel oil, lubricating oil, residual oil, etc.

While the present invention is particularly applicable to the treatment of hydrocarbon fluids, it is understood that it may be employed with other organic fluids which cause deposit formation in heat exchangers as in storage. Such other organic fluids include alcohols, aldehydes, ketones, detergents, pharmaceuticals, organic intermediates, etc.

It is understood that the salt of the present invention may be used along with other additives including, for example, antioxidant, metal deactivator, corrosion inhibitor, detergent, dye, etc. The specific additive to be used will depend upon the particular hydrocarbon oil being treated. 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

A number of different HCl salts of the condensation product of epichlorohydrin and tallow amine were prepared. 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 alkyl amines predominating in 16 to 18 carbon atoms per alkyl group. This 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 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.

The HCl salts of the condensation product formed in the above manner were prepared by reacting a specified concentration of HCl in the form of 0.0951 N alcoholic HCl with different samples of the condensation product. All of these preparations were made by mixing the reactants as stated above at room temperature, with stirring, then heating on a water bath to a temperature of about 95° C., for about 1 hour, followed with which the rest of the alcohol was removed by distillation under water pump vacuum. Additional xylene was then added to each preparation to form a final solution of 50% by weight active ingredient.

The specific details of preparation and certain analytical data are reported in the following table:

<table>
<thead>
<tr>
<th>Additive Number</th>
<th>Gross of condensation product</th>
<th>en. of alcohol</th>
<th>HCl</th>
<th>Percent of amino nitrogen neutralized with HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>31</td>
<td>1.08</td>
<td>1.4833</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>39</td>
<td>2.44</td>
<td>1.4823</td>
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<td>59</td>
<td>3.23</td>
<td>1.4802</td>
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<td>77</td>
<td>4.77</td>
<td>1.4761</td>
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<tr>
<td>5</td>
<td>100</td>
<td>99</td>
<td>9.10</td>
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As heretofore set forth, the above salts were recovered as solutions in xylene of 50% by weight active ingredient. All of these solutions are amber, free-flowing liquids.

Additive 2 had an index of refraction (nD25) of 1.4833. Additive 3 had an index of refraction (nD25) of 1.4833. Additive 4 had an index of refraction (nD25) of 1.4802. Additive 5 had an index of refraction (nD25) of 1.4761.

Example II

As hereinafore set forth, the HCl salts of the present invention are particularly desirable for use to prevent heat exchanger deposits. The different additives prepared as described in Example I were evaluated in the C.P.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 1/2" diameter positioned within an outside tube of 3/4" 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 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 of 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 rate poorer than 3.
The fuel used in these evaluations is a commercial heavy catalytic naphtha and was treated at a tempera-
tude of 400° F. A control sample (not containing an additive) of the naphtha gave a tube rating of 26 when evaluated in the above manner. The results of evaluating the different samples of the naphtha containing the additives described in Example 1 are reported in the fol-
lowing table. The additive was incorporated in a concen-
tration of 0.005% by weight of active ingredient.

<table>
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<th>Additive Number</th>
<th>Tube Rating</th>
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<tr>
<td>None</td>
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<tr>
<td>1</td>
<td>12</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
</tr>
</tbody>
</table>

From the data in the above table it will be noted that the additives of the present invention all served to re-
duce the tube rating to about one-half of that obtained in the absence of the additive. As hereinbefore set for-
th, this serves to reduce deposit formation in heat exchangers.

Example III
The additive of this example is an HCl salt of an ester of the condensation product prepared in the manner de-
scribed in Example I. The ester is the VR-1 acid ester. 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 mixing 63.8 grams of the condensation product pre-
aped as described above, 34.5 grams of VR-1 acid and 100 cc. of xylene. The mixture was heated, with stirring, to a temperature of about 145° C. and refluxed for about 9 hours. The mixture was cooled and distilled under vacuum at about 155° C. to remove the xylene. The product was recovered as a viscous dark liquid and was blended with additional xylene to prepare a solution of 50% by weight active ingredient.

5 grams of the ester solution prepared in the above manner were mixed with 1.6 cc. of 0.0951 N alcoholic HCl and heated, with stirring, to a temperature of about 98° C. for about 1 hour, after which the rest of the alco-
hol was removed by distilling under water pump vacuum. Sufficient xylene was added to form a final solution of 50% by weight active ingredient. This product was a dark brown, opaque, free-flowing liquid, having an index of refraction (nD20) of 1.4867.
The salt prepared in the above manner was evaluated according to the C.F.R. fuel考核 thermal stability test described in Example II. The control sample (not con-
taining an additive) of the oil used in this example had a tube rating of 20. Another sample of the oil containing 0.005% by weight of active ingredient of the salt prepared as described above, when evaluated in this man-
ner, had a tube rating of 12. Here again it will be noted that the additive of the present invention was effective in reducing deposit formation.

Example IV
As hereinbefore set forth, another embodiment of the invention comprises mixed HCl-phosphate salts of the condensation product of epiphthalhydrin with amine. The phosphate salt is the mixed mono- and ditricetyl acid orthophosphate salt of the condensation product prepared as described in Example I. In this preparation, the HCl salt was prepared first and then the phosphate salt was prepared.

100 grams of the 50% active ingredient solution of the condensation product prepared in the manner de-
scribed in Example I and 156 cc. of 0.0951 N HCl solution in isopropanol were commingled at room tempera-
ture and reacted with stirring for 15 minutes. 49.3 grams of mixed mono- and ditricetyl acid orthophosphate were commingled therewith and the mixture heated, with stirring, to 50° C. The mixture then was distilled under water pump vacuum to remove the rest of the alcohol. Sufficient xylene then was commingled with the product to produce a 50% solution ac-
tive ingredient. This solution was recovered as an am-
ber, free-flowing liquid, having an index of refraction (nD20) of 1.4787.
The mixed HCl-phosphate salt prepared in the above manner was evaluated according to the C.F.R. fuel coker thermal stability test described in Example II. The oil used in this example is a commercial J.P.-4 jet fuel and the test was conducted at a temperature of 300° F. A control sample (not containing an additive) of the jet fuel, when evaluated in the above manner, had a tube rating of 34. In contrast, another sample of the jet fuel containing 0.0025% by weight of the mixed HCl-phosphate salt solution (0.00125% by weight of active in-
redient) described above, when evaluated in the above manner, had a tube rating of zero. It is apparent that the additive of the present invention was very effective in reducing deposit formation.

Example V
As hereinbefore set forth, the additive of the present invention also is effective to prevent sediment formation in hydrocarbon oil. The sediment formation will cause plugging of filters, strainers, burner tips, injectors, etc., and the efficacy of the additive is evaluated in a method referred to as the "Erdo 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 very effective additive, the time to reach a differential pressure across the filter of 25 in. Hg is lengthened beyond reasonable limits and the test is stopped after about 300 minutes and the differential pressure at that time is reported. The oil used in this example is the J.P.-4 jet fuel described in Example IV. In this test the preheater was run at 300° F, and the filter at 400° F.

When evaluated in the above manner a control sample (not containing an additive) of the jet fuel developed a differential pressure across the filter of 25 in. Hg in 130 minutes. On the other hand, another sample of this jet fuel containing 0.0025% by weight of the mixed HCl-phosphate salt solution (0.00125% by weight active ingredient) described in Example IV, developed a differential pressure of only 0.05 in. Hg after 300 minutes.

Example VI
The mixed HCl-phosphate salt prepared as described in Example IV also was evaluated in the Erdo test in a commercial J.P.-6 fuel. This test was conducted using a preheater temperature of 400° F. and a filler tempera-
ture of 500° F.
A control sample (not containing an additive) of the J.P.-6 jet fuel, when evaluated in the Erdo test as de-
scribed above, developed a differential pressure of 25 in. Hg in 51 minutes. On the other hand, another sample of the jet fuel containing 0.0025% by weight of the 50% solution (0.00125% active ingredient) of the mixed HCl-phosphate salt prepared as described in Example IV, developed a zero in. Hg pressure after 300 minutes.

At the same time, the preheater tube rating of the mixed HCl-phosphate salt described above was evaluated. A control sample (not containing an additive) of the J.P.-6 fuel had a tube rating of 15. The sample of the J.P.-6 fuel containing the mixed HCl-phosphate salt de-
scribed above had a tube rating of only 6. From the
above data it will be seen that the additive was very effective in preventing filter plugging and tube deposits.

Example VII

The additive of this example is the mixed HCl-phosphosphate salt of an ester of the condensation product of epichlorohydrin and tallow amine. The condensation product was prepared substantially in the same manner as described in Example I. The ester was prepared by refluxing 100 grams of the 50% active solution of the condensation product, 42 grams of oleic acid and 50 cc. of xylene. The refluxing was effected at about 150° C. for 15 hours. An 0.1 N solution of HCl-ethanol is mixed with the ester prepared in the above manner and the mixture is heated, with stirring, at 85° C. for 1 hour. The HCl is used in a concentration to neutralize 10% of the basic amino nitrogen. Mixed mono- and diso-octyl acid orthophosphate is added to the mixture and heated, with stirring, at 50° C. for 40 minutes. Sufficient xylene then is added to produce a final solution of 50% by weight active ingredient.

The mixed HCl-phosphate salt of the ester prepared in the above manner is incorporated in a straight run oil having a boiling range of from about 300° to about 700° F., which oil is passed in heat exchange with hot reactor effluent products. The thus preheated charge then is heated in a furnace at a temperature of 600° F. and passed in contact with alumina-molybdenum oxide-cobalt oxide catalyst to remove sulfur, nitrogen and other impurities from the oil. The reactor effluent products are passed in heat exchange with the charge as described above and then are sent to a separator for the removal of hydrogen and hydrocarbon gases, after which the oil is sent to a fractionating zone to separate a naphtha having an end boiling point of 400° F. and a heavier oil having a boiling range of from about 400° to about 700° F.

I claim as my invention:

1. Hydrocarbon oil containing from about 0.0005% to about 1% by weight of an oil soluble HCl salt of 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 having from about 12 to about 40 carbon atoms per molecule, from about 1% to about 20% of the amino nitrogen in said condensation product being neutralized with HCl.

2. Hydrocarbon oil containing from about 0.0005% to about 1% by weight of an oil soluble HCl salt of the condensation product, formed at a temperature of from about 20° C. to about 150° C., of equimolar amounts of epichlorohydrin and tallow amine, from about 1% to about 20% of the amino nitrogen in said condensation product being neutralized with HCl.

3. Hydrocarbon oil containing from about 0.0005% to about 1% by weight of an oil soluble HCl salt of an ester of carboxylic acid containing 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, from about 1% to about 20% of the amino nitrogen in said condensation product being neutralized with HCl and the amount of carboxylic acid being sufficient to esterify from one to all of the hydroxyl groups in the condensation product.

4. Hydrocarbon oil containing from about 0.0005% to about 1% by weight of an oil soluble mixed HCl-alkyl acid phosphate salt of 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, from about 1% to about 20% of the amino nitrogen in said condensation product being neutralized with HCl and the amount of alkyl acid phosphate being at least one mol of phosphate per mol of the condensation product.

5. Hydrocarbon oil containing from about 0.0005% to about 1% by weight of an oil soluble HCl salt of 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 epichlorohydrin 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, from about 1% to about 20% of the amino nitrogen in said condensation product being neutralized with HCl.

6. Hydrocarbon oil containing from about 0.0005% to about 1% by weight of an oil soluble HCl salt of an ester of stoichiometric amounts of an aliphatic 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 epichlorohydrin 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, from about 1% to about 20% of the amino nitrogen in said condensation product being neutralized with HCl.

7. Hydrocarbon oil containing from about 0.0005% to about 1% by weight of an oil soluble mixed HCl-alkyl acid phosphate salt of the condensation product, formed at a temperature of from about 20° C. to about 150° C., of from 1 to 2 mols of an alkyl amine containing from about 12 to about 40 carbon atoms per molecule with from 1 to 2 mols of an epichlorohydrin 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, from about 1% to about 20% of the amino nitrogen in said condensation product being neutralized with HCl and the amount of alkyl acid phosphate being at least one mol of phosphate per mol of the condensation product.

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