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HYDROCARBON OIL COMPOSITION

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

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

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

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

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

in storage tanks, pipe lines, etc., as well as in the carburetor, fuel lines, etc., used in conjunction with internal combustion engines.

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

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

In a specific embodiment the present invention relates to a method of preventing deposit formation in a heat exchanger through which two fluids at different temperatures are passed which comprises incorporating in at least one of said fluids, in an amount sufficient to prevent deposit formation, a mixture of mono- and dioctyl acid orthophosphate salts of the reaction product of epichlorohydrin with hydrogenated tallow amine.

In still another embodiment the present invention relates to a method of improving burner oil which comprises incorporating therein a stabilizing concentration of a mixture of the mono- and di-tridecyl acid phosphate salts of the reaction product of epichlorohydrin and tallow amine.

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

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

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

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

Illustrative examples of primary alkyl amines include dodecyl amine, tridecyl amine, tetradecyl amine, penta-

decyl 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-amyl-dodecyl amine, N-butyl-tridecyl amine, N-amyl-tridecyl amine, etc. Here again, mixtures of secondary amines are available commercially, usually at a lower price, and such mixtures may be used in accordance with the present invention, provided that the amines meet the requirements hereinbefore set forth. An example of such a mixture available commercially 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, N - hexacosyl-1,3-diaminopropane, N-heptacosyl-1,3-diaminopropane, N-octacosyl-1,3-diaminopropane, N-nonacosyl-1,3 - diaminopropane, N-triacontyl-1,3-diaminopropane, N-hentriacontyl-1,3-diaminopropane, N-dotriacontyl-1,3-diaminopropane, N-tritriacontyl-1,3-diaminopropane, N-tetratriacontyl-1,3-diaminopropane, N-pentatriacontyl-1,3 - diaminopropane, N-hexatriacontyl-1,3-diaminopropane, N - heptatriacontyl-1,3-diaminopropane, N - octatriacontyl-1,3 - diaminopropane, N-nonatriacontyl-1,3-diaminopropane, N-tetracontyl-1,3-diaminopropane, etc. As before, mixtures are available commercially, usually at lower prices, of 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, generally are not preferred. Illustrative examples of such compounds include 1,12-diaminododecane, 1,13-diaminotridecane, 1,14-diaminotetradecane, etc.

In general, it is preferred that the amine compound is a saturated compound and does not contain double bonds in the chain. However, in some cases, unsaturated compounds may be employed, provided they meet the other requirements hereinbefore set forth, although not necessarily with equivalent results. Such amine compounds may be prepared from unsaturated fatty acids and, therefore, may be available commercially at lower cost. Illustrative examples of such amine compounds include dodecylenic amine, diododecylenic 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. In still another embodiment, other suitable nitrogen-containing compounds may be used as, for example, urea, monoethanol amine, etc.

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

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 epidihalohydrin compounds may be utilized. It is understood that the different epihalohydrin compounds are not necessarily equivalent in the same or different substrate 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 of the invention, 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 of the invention, 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 step-wise. 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 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° C. 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 in dilute alcohol 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 hydrogen 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 is completed, the metal halide is removed in any suitable manner, including filtering, 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.

As hereinbefore set forth, the alkyl acid phosphate of the reaction product prepared in the above manner is used as an additive to hydrocarbon oils. 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 ester groups may be attached to the same or different phosphorus atoms. Generally, however, this compound will be symmetrical and, thus, the alkyl ester groups will be attached to different phosphorus atoms.

In general, at least one of the alkyl groups constituting the ester contains at least 6 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 monooctyl 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 orthophosphates, mixture of mono- and dipentadecyl acid orthophosphates, etc.

Preferred alkyl acid pyrophosphates include monooctyl 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 pyrophosphate, 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, ethylbutyl lauryl acid orthophosphate, ethylbutyl capryl acid orthophosphate, ethylbutyl 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 reaction product of epichlorohydrin and amine compound is prepared utilizing at least 1 mol of alkyl acid phosphate per mol of the reaction product and will range up to 1 mol of phosphate per each mol equivalent of basic nitrogen in the reaction product. In general, this will comprise from 1 to about 20 mols of phosphate per 1 mol of reaction product. For example, as hereinbefore set forth, the polymer formed by the reaction of 1 mol of epichlorohydrin with 1 mol of amine compound will contain from about 5 to 10 recurring units, each unit containing a basic nitrogen. Accordingly, from 5 to 10 mols of phosphate are used in order to obtain the desired salt. It is understood that, when the polymer contains more than 10 basic nitrogens, a corresponding larger number of mols of phosphate preferably is used. Thus, in the preferred salt of the present invention, an equivalent mol of phosphate is used per mol of basic nitrogen, although in some cases, an excess or a 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 reaction product 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 undesired reaction which will result in the liberation of water during formation of the salt. 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, 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 per million by weight of the hydrocarbon oil. When used for other purposes, the salt may be used in a concentration of from about 0.0001% to about 1% or more by weight of the hydrocarbon oil. It is understood that the 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 or alumina-molybdenum sulfide-cobalt sulfide. The oil, which may comprise gasoline, kerosene, gas oil or mixtures thereof, is introduced into the process at a temperature of from about ambient to 200° F. and is passed in heat exchange with reactor effluent products being withdrawn at a temperature of from about 500° to about 800° F. The charge is heated by such heat exchange to a temperature of from about 300° to about 600° F., then is heated in a furnace or otherwise to a temperature of from about 625° to about 800° F. and passed with hydrogen in contact with the catalyst. This treatment serves to remove impurities and to hydrogenate unsaturates contained in the charge. Another illustration is a reforming process in which gasoline is contacted with hydrogen in the presence of a platinum-containing catalyst at a temperature of from about 700° to about 1000° F. and the hot effluent product from the reaction zone is passed in contact with the charge in order to cool the former and heat the latter.

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

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

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

When the 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 added to 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, preventing icing, 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 by not with the intention of unduly limiting the same.

Example I

The salt of this example is the mixed mono- and dioctyl acid orthophosphate salt of the reaction product of epichlorohydrin and tallow amine. The reaction 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 or 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. It then was distilled at 160° C. under water pump vacuum to remove the xylene solvent. The product was a white to off-white, hard, brittle solid having a basic nitrogen titration of 3.11 meq./g.

97.95 gms. (0.3 mol equivalent of basic nitrogen) of the reaction product recovered in the above manner was mixed with 54.9 gms. (0.3 mol) of mixed mono- and diisooctyl acid orthophosphate with stirring. The mixing was accompanied with a rise in temperature due to the exothermic heat of reaction. The product then was cooled to room temperature and the salt was recovered as a very viscous, amber colored oil having an index of refraction, N_D^{20}, of 1.4750.

The salt prepared in the above manner was evaluated as a pour point depressant in a commercial S.A.E. 20 Mid-Continent solvent extracted lubricating oil. The salt prepared in the above manner is readily soluble in the lubricating oil in a concentration up to 50% by weight or more.

This lubricating oil, without additive, had an ASTM cold test of 5° F. and an ASTM pour point of 10° F. 1% by weight of the salt prepared in the above manner was incorporated in a sample of the lubricating oil described above and this served to reduce the ASTM cold test down to below —30° F.

Another solution was made to contain 0.5% by weight of the reaction product described above in another sample of the lubricating oil, and this served to reduce the ASTM cold test to —25° F. and accordingly the ASTM pour point down to —20° F.

Furthermore, the sample of lubricating oil containing 0.5% by weight of the salt described above had a viscosity index of 103. In contrast, the lubricating oil without additive had a viscosity index of 98.8.

From the data in the above example, it will be noted that the additive of the present invention served to considerably depress the pour point of the lubricating oil and to increase the viscosity index thereof.

Example II

A salt prepared in substantially the same manner as described in Example I 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 very 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. When evaluated for use as a jet fuel, which normally encounters higher temperature, the test is run at a higher temperature. The preheater is run at a temperature of 400° F. and the filter is run at a temperature of 500° F. The jet fuel, without additive, developed a differential pressure across the filter of 25 in. Hg in 60 minutes. Another sample of this fuel containing 0.005% by weight of the salt described in Example I had a zero differential pressure 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 exceptionally high temperature. Accordingly, the fuel containing additive is satisfactory for use as a jet fuel, whereas plugging difficulties are encountered in the absence of the additive.

Example III

The salt of this example was prepared as the ethyl lauryl acid orthophosphate of the reaction product of epichlorohydrin with tallow amine. Another sample of the reaction product prepared in the manner described in Example I was mixed with the phosphate in the following proportions: 97.95 gms. (0.3 mol equivalent of basic nitrogen) was mixed with 93.18 gms. (0.3 mol) of ethyl lauryl acid orthophosphate with stirring. Here again the reaction mixture increased in temperature due to the exothermicity of the reaction. The product was cooled and the salt recovered as a waxy solvent having a melting range of 38°–44° C.

The salt prepared in the above manner was evaluated as a pour point depressant in another sample of the lubricating oil described in Example I. 1% by weight of the salt served to reduce the ASTM cold test to —20° F. and the ASTM pour point test to —15° F. When compared to the ASTM cold test of 5° F. and pour point of 10° F., it will be noted that the salt was effective in depressing the pour point of the oil.

Example IV

The additive of this example comprises the mixed mono- and di-tridecyl acid orthophosphate salts of the reaction product prepared in the manner described in Example I. 25 gms. of the reaction product were mixed with 9.4 gms. of mixed mono- and di-tridecyl phosphate and reacted for 30 minutes at 50° C. 9.4 gms. of xylene were added to the reaction mixture to form a solution containing 50% by weight of active ingredient.

The salt prepared in the above manner was evaluated according to the C.F.R. fuel coker thermal stability test. In this test, the oil heated to the specified temperature is passed through the annular space surrounding a heated inside tube of 17" length and ½" diameter positioned within an outside tube of 9/16" inside diameter. The inside tube is heated by means of a heating coil positioned therein to a temperature of either 300° or 400° F. depending upon the particular fuel being evaluated. The test is conducted for 300 minutes, at a pressure of 160 pounds per square inch, and a flow rate of 6 pounds of fuel per hour. Following the run the equipment is dismantled, 13" or less of the inner tube is marked off in 1" increments and the deposits on the outside surface of the heated inner tubes 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.

The fuel evaluated in this example is a J.P.–6 commercial fuel and was tested at 400° F. A sample of the jet fuel evaluated in the above manner had a tube rating of 15. 25 parts per million by weight of the salt described above was incorporated in another sample of this fuel and, when evaluated in the above manner, the tube rating was 6. No 1" increment rated higher than 2.

It will be noted that the reaction product of the present invention served to considerably reduce deposit formation.

Example V

Another sample of the salt prepared as described in Example IV was evaluated in the "Erdco Test." The fuel, without additive, developed a differential pressure of 25 in. Hg in 51 minutes. In contrast, a sample of the fuel containing 25 parts per millon by weight of the salt described in Example IV exhibited no increase in differential pressure after 300 minutes. Here again it will be noted that the salt of the present invention was very effective in retarding deposit formation.

Example VI

The salt prepared in the manner described in Example IV also was evaluated as a corrosion inhibitor. In this evaluation, which is a modified M.I.L.–I.25017 procedure, 300 cc. of depolarized isooctane, to which 30 cc. of synthetic sea water is added, is placed in a beaker open to the atmosphere. A steel strip of $\frac{1}{1000}$" thickness and ⅛" wide is welded to a similar strip enclosed in a glass tube. The probe then is suspended in the mixed oil-water suspension, heated to and maintained at 100° F. for 20 hours. The extent of corrosion is determined by measuring the loss in conductivity which in turn is converted to loss of steel, reported as micro inches penetration. When a blank or control sample of the oil-water emulsion is evaluated in the above manner, the corrosion is reported as about 150 micro inches penetration. In contrast, in another evaluation in which 60 parts per million of the salt described in Example IV was incorporated in the oil-water suspension, no loss in conductivity and accordingly no corrosion was recorded.

Example VII

The salt prepared in the manner described in Example I is used in a commercial Unifining Unit to prevent heat exchanger deposits. In this unit gasoline is subjected to hydrotreating in the presence of an alumina-molybdenum oxide-cobalt oxide or alumina-molybdenum sulfide-cobalt sulfide catalyst. The gasoline charge is introduced at a temperature of 200° F. and is passed in heat exchange with reactor effluent being withdrawn at a temperature of about 675° F. This serves to heat the charge to a temperature of about 550° F. and to cool the reactor effluent to a temperature of about 325° F. In this unit the charge is passed through the tubes of the exchanger and the reactor effluent is passed through the shell. 15 parts per million by weight of the salt is incorporated in the gasoline before the same is passed into the exchanger and this serves to prevent heat exchanger deposits and to permit extended use of the heat exchanger without requiring shutting down the plant because of the plugging of the heat exchanger tubes.

Example VIII

The salt of this example is prepared as follows: Separate solutions of epichlorohydrin and of dioctadecyl amine are prepared. One-half mol proportion of the amine solution is reacted with the epichlorohydrin solution at a temperature of 60° C. for 3 hours. Then the other half mol proportion of amine is added gradually to the reaction mixture, stirred and reacted at 75° C. for 3 hours. One mol proportion of sodium hydroxide then is added with stirring and heating to 85° C. for 4 hours. Following completion of the reaction, the mixture is cooled, filtered and recovered as a solution in xylene. To this mixture is added didecyl acid pyrophosphate, in a concentration of ½ mol of phosphate per each mol equivalent of basic nitrogen in the first mentioned reaction product, and the mixture is reacted at room temperature, with stirring, for 2 hours to form the salt.

Example IX

The salt prepared in the manner described in Example I was evaluated as a deicer in gasoline. This evaluation was effected in a simulated test in which 100 ml. of a heptane fraction and 40 ml. of water are stirred in a Waring Blendor having a polished steel beaker inserted in the top of the blender. The additive, when used, is incorporated in the heptane fraction before being placed in the blender. The Waring Blendor is run for one minute and then 50 gms. of powdered Dry Ice is added to the acetone, usually over a period of 10 seconds. The Waring Blendor is then run for an additional one minute. The ice deposited in the beaker is weighed.

In a run made in the absence of an additive, 24 gms. of ice were recovered. In another run in which 0.1% by weight of the salt described above was incorporated in the heptane fraction, only 11 gms. of ice were recovered. In another run in which 0.25% by weight of the salt described above was incorporated in the heptane fraction, the amount of ice recovered was only 7 gms.

From these data it will be noted that the additive of the present invention was effective in decreasing ice formation.

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 the reaction product of an aliphatic amine containing from 12 to about 40 carbon atoms per molecule with an epihalohydrin compound selected from the group consisting of epichlorohydrin, 1,2-epi-4-chlorobutane, 2,3-epi-4-chlorobutane, 1,2-epi-5-chloropentane, 2,3-epi-5-chloropentane and corresponding bromo and iodo compounds, the phosphate of said salt being selected from the group consisting of mono-alkyl and dialkyl acid orthophosphates and pyrophosphates.

2. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an alkyl acid phosphate salt of the reaction 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 12 to about 40 carbon atoms per molecule with from 1 to 2 mols of an epihalohydrin compound selected from the group consisting of epichlorohydrin, 1,2-epi-4-chlorobutane, 2,3-epi-4-chlorobutane, 1,2-epi-5-chloropentane, 2,3-epi-5-chloropentane and corresponding bromo and iodo compounds, said salt having been formed by first removing halogen from said reaction product and then reacting with the latter from 1 to 20 mols of alkyl acid phosphate per mol of reaction product at from room temperature to about 200° C., said phosphate being selected from the group consisting of mono-alkyl and dialkyl acid orthophosphates and pyrophosphates.

3. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an octyl acid orthophosphate salt of the reaction product, formed at a temperature of from about 20° C. to about 150° C., of from 1 to 2 mols of tallow amine with from 1 to 2 mols of epichlorohydrin, said salt having been formed by first removing chlorine from said reaction product and then reacting with the latter from 1 to 20 mols of said phosphate per mol of reaction product at from room temperature to about 200° C.

4. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of a mixture of mono- and dioctyl phosphate salts of the reaction product, formed at a temperature of from about 20° C. to about 150° C. of from 1 to 2 mols of hydrogenated tallow amine with from 1 to 2 moles of epichlorohydrin, said salts having been

formed by first removing chlorine from said reaction product and then reacting with the latter from 1 to 20 mols of said phosphates per mol of reaction product at from room temperature to about 200° C.

5. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of mono- and di-tridecyl acid orthophosphate salts of the reaction product, formed at a temperature of from about 20° C. to about 150° C., of from 1 to 2 mols of tallow amine with from 1 to 2 mols of epichlorohydrin, said salts having been formed by first removing chlorine from said reaction product and then reacting with the latter from 1 to 20 mols of said phosphates per mol of reaction product at from room temperature to about 200° C.

6. Hydrocarbon oil containing from about 0.0001% to about 1% by weight of an octyl acid orthophosphate salt of the reaction product, formed at a temperature of from about 20° C. to about 150° C., of from 1 to 2 mols of dioctadecyl amine with from 1 to 2 mols of epichlorohydrin, said salt having been formed by first removing chlorine from said reaction product and then reacting with the latter from 1 to 20 mols of said phosphate per mol of reaction product at from room temperature to about 200° C.

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