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3,558,470

ANTIFOULANT PROCESS USING PHOSPHITE AND ASHLESS DISPERSANT

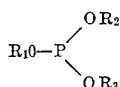
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No Drawing. Continuation-in-part of application Ser. No. 694,039, Dec. 28, 1967. This application Nov. 25, 1968, Ser. No. 778,751

Int. Cl. C10g 9/16; C10l 1/26; C23f 14/00
U.S. Cl. 208—48 13 Claims

ABSTRACT OF THE DISCLOSURE

Mineral hydrocarbon feedstocks which are subjected to elevated temperatures of the order of 200° to 1300° F. and which have a tendency to form deposits by reason of such heating have added thereto minor amounts, of the order of 1 to 400 parts per million by weight, as a pretreatment, of a condensation product of a long chain alkyl or alkenyl monocarboxylic acid, dicarboxylic acid or anhydride thereof, having a number average molecular weight between about 600 and about 5000, and at least one polyalkylene polyamine and an additional small amount of a phosphorous acid or a mono-, di- or tri-organic phosphite ester having the formula:



wherein R₁ is hydrogen or a hydrocarbon radical such as alkyl, aryl, alkaryl, cyclo alkyl, alkenyl, aralkyl or simple chlorinated substituents thereof and R₂ and R₃ are hydrogen or are selected from the same group as shown for R₁. Best antifoulant results are obtained where the condensation product and the phosphorous compound as admixtures or as the prereacted compound of these two types of additives are added to those feedstocks which contain oxidized hydrocarbons and/or unsaturated hydrocarbons.

RELATED APPLICATION

This application is a continuation-in-part of copending application Ser. No. 694,039, filed Dec. 28, 1967, now abandoned.

DESCRIPTION OF THE INVENTION

The present invention is concerned with a method for reducing or preventing the usual fouling of process equipment customarily and conventionally employed in the processing of crude oil or various fractions of crude oil as well as the processing of cuts and fractions recovered from certain processes which have altered the constituents of petroleum. Almost all crude oil and fractions thereof, as well as various process cuts produced from the same, contain minor amounts of easily oxidizable and oxidized hydrocarbon constituents or, particularly, if chemical reactions or thermal treatment have been involved, the resultant fractions contain either small or moderate

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amounts of olefinic constituents. Additionally, almost all crude oils contain minor amounts of dissolved oxygen, metals and sulfur either in the free state or chemically combined, or both. Furthermore, as is commonly required, most refinery process equipment is fabricated out of steel or iron so that continued passage of petroleum fractions either initially or after processing treatments in such equipment is bound to cause these streams to contain minor amounts of iron or iron compounds.

One of the most troublesome phenomena that occur involves the severe fouling of petroleum process equipment particularly that used in the distillation, cracking, visbreaking, and hydrogenation operations. This fouling problem is a serious one because for the most part almost all unit processes involve the use of one or a plurality of heat exchangers which, with continued use, customarily suffer decreases in efficiency and heat transfer, increased pressure drops, and loss of throughput. These difficulties arise because of the troublesome deposition of inorganic and organic deposits on the inner surfaces of such equipment by reason of the presence of unstable constituents such as the oxidized derivatives of hydrocarbons, the inorganic impurities present in the hydrocarbon fractions and/or the presence of olefinic unsaturated hydrocarbons or their polymeric derivatives. The processing of such feedstocks containing one or more of these unstable constituents results in the deposition of these materials as oil-insoluble polymers and complexes to the extent that periodically such process units must be shut down. This fouling of furnaces, pipes, heat exchangers, reboilers, and condensers is costly from the standpoint of the necessary shut down time involved with consequent loss of production as well as from the need for the expenditure of man-hours for the disassembling, cleaning, and reassembling of the various items that make up the process unit.

If some method could be devised for excluding oxygen from contact with the various hydrocarbons or if some method could be devised to prevent the formation of polymers and their subsequent deposition as well as other depositions as heretofore described, as foulants, many thousands of dollars could be saved and the resulting improvement in efficiency of the process equipment should be most welcome. Floating roof tanks and use of "inert" gas blanketing have been employed in the past in efforts to exclude molecular oxygen from contacting the various mineral hydrocarbon fractions and crude oils but they do not completely prevent oxygen contact. The use of an antifoulant as a pretreatment for the feedstocks being processed in the petroleum refineries has been proposed in the past. This could be the solution to this problem of high maintenance cost and, for example, lowered heat exchanger efficiency and the like. Various types of antioxidants have been employed for this purpose with varying degrees of success.

The present invention is directed to the use of an ashless dispersant coupled with the use of a phosphite type antioxidant-antipolymerizant compound either as an admixture or as the reaction product of these two types of materials. The use of these two types of materials, in combination as a chemical reaction product or admixture, has unexpectedly proven to give a higher degree

of antifoulant character when added to feedstocks which normally tend to deposit oil-insoluble components and scale, than has heretofore been attainable. Apparently, through the use of such a combination of additives the polymerization and other depositions leading to generation of oil-insoluble materials is significantly reduced or prevented. The inorganic deposits, thus being devoid, *inter alia*, or polymeric binder associated with them, do not have as great a tendency to settle out or coat the inner surfaces of the process equipment. The fouling is controlled to such an extent that the usually required shut down for cleaning the heat transfer surfaces is reduced to a minimum and, often times, avoided altogether.

The presence of the antioxidants-antipolymerizants, *i.e.*, the phosphite type materials, is believed to inhibit the formation of polymers or oxidized polymers. Their use has been found to be superior to prior art antifoulants such as the high molecular weight amino or amido compounds, specifically when used in association with or reacted with organic ashless dispersants which are prepared by the condensation of polyalkylene polyamines with the high molecular weight alkyl or alkenyl mono- or dicarboxylic acids or anhydrides thereof.

The ashless dispersants, and their methods of manufacture are well known and such dispersants are commercially available at the present time. They are used principally in lubricating oils for the purpose of controlling sludge formed in such oils during use. They are also known to have been previously used in connection with middle distillate fuels particularly the heating oils for the purposes of improving flow ability under ambient low temperature conditions. Likewise, the phosphite esters and phosphorous acid reaction products employed herein have been used in middle distillate fuels for the purpose of their antioxidant effect. The condensation products, *i.e.*, the materials heretofore known as ashless dispersants, are oil-soluble and have a number average molecular weight ranging between about 600 and about 5000 and by themselves when added to the aforementioned type of feedstock may show some antifoulant activity. The phosphite esters or phosphorous acid when added alone to the feedstocks of the above-described types do not effectively serve as an antifoulant in spite of their antioxidantizing character. It is surprising therefore to have discovered that a combination of the two types of additives either as admixtures or as reacted products obtained from reacting the two types with each other, when incorporated into the mineral hydrocarbon feedstocks having a tendency to form oil-insoluble deposits under elevated temperatures, tended to minimize both the rate of formation of such deposits and the total amount of such deposits formed.

The combined addition of organic ashless dispersants and the phosphite esters, or phosphorous acid, in admixture or chemically combined with each other to the feedstocks which are to be subjected to elevated temperature conditions, *inter alia*, during refinery processing operations, results in the marked diminution of deposits for prolonged periods of time, thus virtually eliminating the necessity for shutting down refinery processing units for the purpose of removing fouling deposits and thus allowing for greater production per unit. Further, there are associated savings in labor costs and mechanical costs. It will be appreciated that these savings come about due to the elimination of the necessity for frequent "turn arounds."

It has been previously suggested and taught by U.S. Pat. No. 3,235,484, and its Reissue Pat. 26,330, that carbonaceous materials are inhibited as to their formation in refinery processes when the hydrocarbon feedstocks have added thereto a small amount of an oil-soluble high molecular weight acylated amine prepared by mixing a long chain high molecular weight alkenyl or alkyl succinic

acid or succinic acid anhydride with a polyalkylene polyamine. Also, U.S. Pat. 3,364,130 shows similar uses for condensation products of the same type but using monocarboxylic acids instead of dicarboxylic acids.

The condensation product, *i.e.*, amides or imides of the high molecular weight alkyl or alkenyl mono or dicarboxylic acid or anhydrides thereof with a polyalkylene polyamine plus the phosphite ester, phosphorous acid or reaction products obtained by reacting the two type together, it has been discovered, markedly reduces the tendency to produce fouling as well as reduces the total amount of fouling per unit of time in the thermal treatments of a great many different types of mineral oil feedstocks and fractions. Many normally liquid mineral hydrocarbon mixtures containing molecular oxygen, inorganic impurities, sulfur, sulfur compounds, and/or monolefinic constituents have the decided tendency to form polymers, scale, and so forth, *i.e.*, oil-insoluble contaminants and deposits generically referred to as fouling deposits, particularly upon the surfaces which such feedstocks contact when they are subjected to superatmospheric temperatures. Since all hydrofining, cracking, reforming, visbreaking, *etc.* of such mixtures, whether catalytic or only thermal, are conducted at temperatures above 200° F. and generally at temperatures between about 300° and about 1300° F., all feedstocks to such operations, have the tendency to produce fouling deposits, in such processing units at the places where heat transfer occurs. Typical refinery feedstocks are not limited to those specifically named but include also those used to produce catalytically reformed naphtha, virgin naphthas, crudes, reduced crudes, hydrofined feedstocks of all types, light gas oils, heavy gas oils, recycle feedstocks in reforming and catalytic cracking operations, delayed coker feedstocks, recycle gas oil, heavy thermal gas oils, light catalytic cycle oil, steam cracked naphthas, gas oils and all other feedstocks containing significant amounts of impurities heretofore mentioned.

One component of the antifoulant compositions used in the present invention is the dispersant type condensation product of a high molecular weight alkyl or alkenyl substituted mono or dicarboxylic acid or anhydride thereof and a polyalkylene polyamine, the condensation being effected under conditions which cause the formation of amides, imides, *etc.* These dispersants are characterized by a long chain hydrocarbon group, or groups, attached to the acid, so the acid contains a total of about 50 to 250 carbon atoms, said acid being attached to the amine either through salt, imide, amide, or ester groups. Usually, these dispersants are made by condensing a monocarboxylic acid or a dicarboxylic acid, preferably a succinic acid producing material such as alkenyl succinic anhydride, with an amine or polyamine.

The polyamine can be condensed with the acid or anhydride using equal molar proportions of the acid and the polyamine or a molar excess of the acid over that of the polyamine can be used. The amount of acid used in the reaction should be sufficient to react with at least one amino group per molecule of polyamine but it may range up to sufficient acid to react with each amino group present per molecule of the polyamine. Preferably, the polyamine is a polyalkylene polyamine having from 3 to 8 amino groups and the proportion of carboxylic acid to amine ranges from about 1 to about 5 moles of acid per mole of polyamine. The acid is reacted with the alkylene polyamine at a temperature of about 200° to about 400° F. so as to drive off water that is split out during the reaction. The evolved water is readily removed by blowing an inert gas such as nitrogen through the reaction mixture during the course of the reaction. Generally, temperatures in the range of 250° to 350° F. will adequately bring about the reaction. For example, heating may be conducted at from 6 to 20 hours at 275° to 320° F.

Carboxylic acids or their anhydrides for use in the present invention will have molecular weights in the range of about 600 to about 5000, preferably from about 700 to about 3000. Such acids can be prepared by oxidizing high molecular weight olefins, for example, polyisobutylene of about 900 molecular weight, with an oxidizing agent such as nitric acid or oxygen, by addition of an aldehyde to an olefin followed by oxidation of the adduct, or by addition of halogen to a high molecular weight olefin to form a halogen compound followed by hydrolyzing and oxidation of the latter. Some of these procedures are taught in British Pat. No. 983,040.

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

Monocarboxylic acids can also be prepared from olefin polymers such as a polymer of a C_2 to C_5 monoolefin, e.g., polypropylene or polyisobutylene, halogenating the polyolefin and then condensing it with an unsaturated monocarboxylic acid such as acrylic acid. Examples of suitable olefin polymers include polyethylene, polypropylene, or polyisobutylene, having an average molecular weight of about 600 to 5000, preferably 700 to 3000. Polyisobutylene is preferred, since it has a lessened tendency to gel the product, as compared to some of the other polyolefins such as polyethylene and polypropylene. The polymer is halogenated by contacting the polymer with either bromine or chlorine, preferably by blowing chlorine through the polymer to provide about one to two atoms of halogen per molecule of polymer. The halogenation step may be conducted in the temperature range of from about 50 to about 300° F. To aid in the halogenation step, the polymer may be dissolved in a suitable solvent, such as carbon tetrachloride, in order to lower the viscosity of the polymer. However, the use of such a solvent is not necessary.

The time required for halogenation may be varied to some extent by the rate at which the halogen is introduced. Ordinarily from about 2 to about 5 hours is a satisfactory halogenation period. In a representative plant scale operation involving the chlorination of polyisobutylene of 830 molecular weight, a 100-pound batch will be chlorinated with 10 pounds of chlorine introduced into the reactor over a period of 3.5 hours using a chlorination temperature of about 250° F.

The halogenated polymer thus obtained is condensed with an alpha-beta unsaturated, monocarboxylic acid of from 3 to 8 carbon atoms. Ordinarily, because of their greater availability, acids of this class having 3 to 4 carbon atoms will be used. Such acids include acrylic acid, alpha-methyl-acrylic acid (i.e., 2-methyl propenoic acid) and crotonic or isocrotonic acid (beta-methylacrylic acid). Other alpha-beta unsaturated acids that may be employed include tiglic acid (alpha, methylcrotonic acid), angelic acid (alpha, methylisocrotonic acid), sorbic acid, and cinnamic acid. Esters of such acids, e.g., ethyl methacrylate, may be employed if desired in place of the free acid.

In condensing the halogenated polyolefin with the unsaturated acid, at least one mole of acid is used per mole of halogenated polyolefin. Normally, the acid will be employed in excess and may amount to as much as 1.5 to 2 moles per mole of halogenated polyolefin. The condensation temperature may be in the range of from about 300° to 500° F. and will preferably be within the range of from about 375° to about 475° F. The con-

densation may require from about 3 to about 24 hours, but will ordinarily take place in from 6 to 18 hours. After the reaction has been completed, excess acid may be purged from the mixture, for example, by blowing with a stream of nitrogen at a temperature of 400° to 500° F.

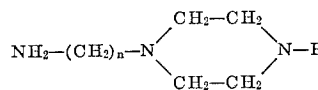
High molecular weight olefinic carboxylic acids of this type may also be prepared by a so-called one-step process involving the halogenation of the olefin polymer in the presence of the alpha-beta unsaturated acid. Using proportions of reactants within the ranges discussed above, the starting acid and the olefin polymer are mixed together in the reactor, the temperature being kept below about 150° F. until the start of halogen introduction so as to avoid homopolymerization of the alpha-beta unsaturated acid. Once halogenation has begun, the temperature may be raised to as high as 250° F. After halogen introduction, the temperature may be raised to 300° to 500° F. to effect the condensation reaction.

The dicarboxylic acids or their anhydrides used have alkenyl or alkyl groups substituted therein and are most commonly composed of from 40 to 250 carbon atoms per alkenyl or alkyl radical. Their methods of preparation are well known and are fully disclosed, for example, in U.S. Pats. 3,219,666; 3,172,892 and 3,272,746. Briefly, they are formed by the reaction of a polymerized C_2 to C_5 alpha monoolefin, such as polypropylene, polyisobutylene, ethylene-propylene copolymers, etc., either chlorinated or as the unsubstituted olefinic polymer, with an alpha-beta unsaturated dicarboxylic acid or anhydride thereof, such as acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, sorbic acid, fumaric acid, maleic acid, maleic anhydride, succinic anhydride, and the like. The ratio of the reactants and the reaction conditions are well known and conventionally employed as evidenced by the disclosures contained in the aforementioned U.S. patents. Generally one to one mole ratios of chlorinated polymers and the acids are employed.

The aliphatic polyamine that is employed in preparing the reaction products of the present invention can be a polyalkylene polyamine having the following general formula:



where n is 2 to 4 and m is a number from 0 to 10. Specific compounds coming within the formula include diethylene triamine, triethylene tetramine, tetraethylene pentamine, dibutylene triamine, dipropylene triamine, hexaethylene heptamine, octaethylene nonamine, and tetrapropylene pentamine. N,N' -di-(2-aminoethyl)ethylene diamine may also be used. Other aliphatic polyamine compounds that can be used include the N -aminoalkyl piperazines of the formula:

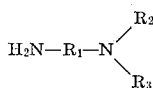


wherein n is a number from 1 to 3, and R is hydrogen or an aminoalkyl radical containing 1 to 3 carbon atoms. Specific examples include N -(2-aminoethyl) piperazine, N -(2-aminoisopropyl) piperazine, and N,N' -di-(2-aminoethyl) piperazine.

Still other alkylene amino compounds that can be used include dialkylamino alkyl amines such as dimethylamino

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methyl amine, dimethylamino propyl amine, methylpropyl-amino amyl amine, etc. These can be characterized by the formula:

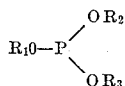


wherein R_1 is an alkylene radical, e.g., an ethylene, propylene, or butylene radical, and R_2 and R_3 are C_1 to C_5 alkyl radicals.

Thus, the alkylene polyamine or aliphatic polyamine compounds used in this invention can be broadly characterized as alkylene amino compounds containing 2 to 12 nitrogen atoms wherein pairs of nitrogen atoms are connected by alkylene groups of from 2 to 4 carbon atoms. Mixtures of polyalkylene polyamines, dialkylamino alkyl amines, mixtures of N-aminoalkyl piperazines, and mixtures of the polyalkylene polyamines with the N-aminoalkyl piperazines can also be used.

The phosphite ester or phosphorous acid additive employed in association with the high molecular weight condensation products may be either a mono-, di- or tri-ester or mixtures of two or more of these three types of esters or phosphorus acid or mixtures of phosphorus acid and one or more phosphite esters. The organic substituent employed in the ester formation and which is generally obtained from the respective monohydric alcohol or phenol, in the conventional manner, is a hydrocarbon or chlorinated hydrocarbon. All that is required is that it be a phosphite ester and that it be oil soluble, i.e., soluble in hydrocarbon feedstocks to which it is added. In view of the fact that no critical amount other than a maximum of about 400 parts per million by weight concentration is employed in the feedstock, the degree of oil solubility of the phosphite ester or phosphorous acid does not have to be great, it being only necessary that up to this amount of material should dissolve in the hydrocarbon feedstock.

The phosphite component may be represented by the formula:



wherein R_1 is hydrogen or a hydrocarbon radical selected from the group consisting of alkyl, chloralkyl, aryl, chlor-aryl, alkaryl, chloralkaryl, cycloalkyl, chlorcyclo alkyl, alkenyl, chloralkenyl, aralkyl, and chloraralkyl; and wherein R_2 and R_3 are each hydrogen or selected from the same group as R_1 .

The total number of carbon atoms for each of R_1 , R_2 and R_3 ranges between about 1 and about 50 with the preferred range being between about 8 and about 20 carbon atoms per hydrocarbon radical. Typical examples of the phosphite esters and phosphorous acid are the following specific phosphite compounds (the specific listing of the monoester is intended to include the like listing of the corresponding di- and tri-ester as well; thus, for example, methyl phosphite is intended to include dimethyl phosphite and trimethyl phosphite but in instances where the R_1 , R_2 and R_3 are not the same, the di- and tri-esters are set forth in full). They are: phosphorous acid; methyl phosphite; ethyl phosphite; n-propyl phosphite; isopropyl phosphite; butyl phosphite; pentyl phosphite; hexyl phosphite; cyclohexyl phosphite; heptyl phosphite; nonyl phosphite; decyl phosphite; lauryl phosphite; lorol phosphite; cetyl phosphite; octadecyl phosphite; heptadecyl phosphite; phenyl phosphite; alpha or beta naphthyl phosphite; alpha or beta naphthenyl phosphite; benzyl phos-

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phite; tolyl phosphite; methyl, phenyl phosphite; dimethyl, phenyl phosphite; amyl, phenyl phosphite; diamyl, phenyl phosphite; nonylphenyl phosphite; nonyl, phenyl phosphite; 4-amylphenyl phosphite; 4-amylphenyl, diethyl phosphite; di-octadecyl di-phenyl phosphite; octadecyl di-phenyl phosphite; isobutyl phenyl phosphite; nonyltolyl phosphite; nonyl, ditolyl phosphite; polyisobutenyl di-phenyl phosphite; di-polyisobutenyl phosphite; di-polyisobutenylphenyl phosphite; polyisobutenylphenyl phosphite; chlorethyl phosphite; chlorbutyl phosphite; chloroctyl phosphite; chlorphenyl phosphite; chlorbenzyl phosphite; chloritolyl phosphite; chlorpolyisobutenyl, diphenyl phosphite; di-(chlorpolyisobutenyl) ethyl phosphite; di-polyisobutenyl, chlorbenzyl phosphite; di-polyisobutenyl, chlorpolyisobutenyl phosphite.

Many of these esters employed, particularly those containing the smaller number of carbon atoms per molecule, are readily available commercially and their methods of preparation are conventional. Some of the esters, particularly those having the longer alyl chains or hydrocarbon radicals or chlorinated hydrocarbon radicals of the higher number of carbon atoms per radical, although presently not available commercially, are readily prepared by reacting one, two, or three moles of the corresponding alcohol or phenol with each mole of phosphorus trihalide such as phosphorus trichloride or phosphorus tribromide. This is a conventional reaction and while there are other ways, also conventional, of producing these various phosphite esters, the present invention is not concerned with the particular method by which the phosphite esters are produced. In those cases where mono- or di-esters are formed, it is sometimes desirable, following the esterification reaction, to treat the reacted mixture with water, dilute aqueous lyze off the residual chlorine or bromine atoms present by reason of the particular trivalent phosphorus compound employed as an original reactant. The hydrolysis of a phosphorus trihalide yields phosphorus acid also.

Only relatively small amounts of the amide dispersant and the phosphite esters are required in order to produce outstanding results in the reduction of fouling deposits and in the formation of such fouling deposits. In general, the combined amount of the two types of additives does not need to exceed about 400 parts per million (p.p.m.) by weight based on the total feedstock compositions. Larger amounts than 400 p.p.m. may be employed but this is simply less desirable because the possible increased antifouling effect is not sufficiently great to warrant the use of larger amounts of these additives and such practice simply constitutes an extravagance. In general, and for best results, a weight ratio of amide dispersants to phosphite esters ranging between about 1:1 and about 20:1, preferably between about 4:1 and about 8:1 is employed. The preferred number average molecular weight of the amide dispersants is generally between about 800 and about 2500.

As before set forth, admixtures of the ashless dispersant condensation products may be admixed with the selected phosphite esters and/or phosphorous acid and used as such. The instant novel additives, however, also encompass the reaction products of such condensation products with the phosphite material (which includes phosphorous acid). Also, if desired, the polyalkylene polyamine may be initially reacted with the phosphite material and that reaction product reacted with the mono or dicarboxylic acid to produce a reacted condensation product-phosphite type additives. All these components may be admixed and then reacted as well. All of the types of reactions are carried out in the liquid phase either in the absence of or presence of inert solvents which are normally inert liquid petroleum or organic solvents, petroleum ether, hexane, heptane, benzene, toluene, middle distillate petroleum fractions, such as kerosene, reduced crude, etc., or fractions and treated cuts of crude oils which constitute the feedstocks to which such antifoulant additives are to be

added. Temperatures of reactions employed will generally range between about 0° and about 120° C., preferably between about 50° and about 100° C. Reaction times will vary between about 1 and about 20 hours, preferably between about 3 and about 10 hours. The reaction solvent, if desired, may be removed from the reacted mixture by distillation under vacuum, atmospheric, or superatmospheric pressure.

Other antifoulants, as well as other types of additives, may also be used in conjunction with the novel additives herein described. Representative of these additives, some of which have been used in the past, for this same purpose, are phenyl alpha naphthylamine and the various types of amino alkylphenols such as the condensation product of C₁-C₃ aldehydes, C₂-C₅ alkylene diamines and alkylphenols having C₄-C₁₆ alkyl groups. These latter products are formed for instance by the condensation of two moles of formaldehyde, one mole of nonylphenol and one mole of ethylene diamine. Additionally, some of the commercial antifoulant additives which heretofore have been employed are the ethanol amine still bottoms, i.e., bottoms remaining after the distillation of monoethanol amine, from the reacted mixture, which are then reacted with iso-oleic acid; the long chain alkyl amide phosphate of the diethyl ester of phosphoric acid, the polymethylmethacrylates, and the iso-oleic acid amide of tetraethylenepentamine, and the like.

The following examples are intended to illustrate the invention but it is not intended that the invention be limited thereto.

EXAMPLE 1

A 110-pound portion of polyisobutylene of 780 molecular weight was heated to 250° F., then a stream of chlorine was passed through the heated polyisobutylene at the 250° F. temperature at a rate of 2.5 pounds of chlorine per hour for a total of 4 hours, the total chlorine treat thus being 10 pounds. A sample of the chlorinated product analyzed 4.3% chlorine and the product had an API gravity of 23.3. To the chlorinated polyisobutylene there was added 10.5 pounds of acrylic acid. Over a period of two hours, the temperature was raised from 250° F. to 425° F. and the pressure was increased to 20 p.s.i.g. Heating was continued for 5 hours at 425° F. and the reaction vessel was vented to maintain the pressure of 20 p.s.i.g. The pressure was then released and the mixture was purged with nitrogen for 2 hours to remove unreacted acrylic acid. The polyisobutenyl propionic acid thereby obtained at the end of the reaction weighed 109.3 pounds, had a molecular weight of about 800 and a total neutralization number (ASTM D-664) of 46.2 milligrams of KOH per gram. The chlorine content was found to be 0.3 wt. percent.

To this material, there was added 3.38 pounds of tetraethylenepentamine and the reaction mixture was heated at 300° F. for 9 hours at a reduced pressure while purging the reacting mixture with a stream of nitrogen during the entire 9 hours period to remove water or other low boiling material as it was formed. The condensation product was then placed in kerosene so as to form, by weight, a 50/50 volume percent mixture.

Tris(nonylphenyl)phosphite was prepared by reacting three mols of nonylphenyl, purchased on the open market, with one mol of phosphorus trichloride under reflux conditions and until no further amounts of hydrogen chloride were evolved.

EXAMPLE 2

28 grams of phosphorus trichloride were hydrolyzed with 11 grams of water at room temperature. After all hydrogen chloride had ceased to be evolved, as a result of

this hydrolysis, 142.8 grams of ethylene dinitrilo tetraethanol [N,N,N',N'-tetrakis (ethylol) ethylenediamine] were added to the mixture. Three cc. of water were collected after 8 hours. 56 grams of the above material were reacted with 500 grams of polyisobutenyl succinic anhydride (mol. wt. about 900). About 4.5 cc. of water were collected at 110° C. after 8 hours. The product analyzed 0.32 wt. percent phosphorus and 1.28 wt. percent nitrogen. A solvent neutral paraffinic oil of about 150 SUS at 100° F., was added to the resultant reactant product in order to give about a 70% active ingredient concentration.

EXAMPLE 3

A mixture of 500 grams of polyisobutenyl succinic anhydride, 540 grams of a lubricating oil which served as a liquid reaction medium and was a solvent extracted neutral paraffinic fraction having a viscosity of about 150 SUS at 100° F. and about 35 grams of tetraethylenepentamine was heated to 120° C. for 4 hours. At the conclusion of this reaction, 11.0 grams of phosphorus acid was added to the mixture and heated at the same temperature for an additional 4 hours. The final product oil concentrate had a nitrogen content of 1.0% and a phosphorus content of 0.38%. It contained about 50% of active ingredient based on the total oil concentrate composition.

EXAMPLE 4

625 grams of a 70% oil concentrate of the product of condensing polyisobutenyl succinic anhydride with tetraethylenepentamine (reacted in the ratio of 2.8 moles of anhydride per mole of polyamine) was admixed with 100 grams of diethyl phosphite and was heated at 100° C. for 2 hours. It was thereafter stripped with a nitrogen gas current for 1 hour.

EXAMPLE 5

Several runs were carried out in which varying amounts of additives obtained as described in several of the above examples were employed in various types of feedstocks and the compounded admixtures were subjected to a 250 to 300 minute Erdco CFR Coker Test which is described in detail in the Frazier et al. article in the Oil and Gas Journal for May 3, 1965, vol. 63, pp. 117-122. As described in the article, each test was carried out by preparing a five gallon sample of the feedstock and adding thereto the designated amount of the particular additive or additives used in the test. All additive concentrates were diluted with an equal volume of kerosene before addition to the feedstocks. Upon running the feedstocks through the apparatus shown in FIG. 1 of the article under the test conditions set forth in the article and after measuring the pressure drops across the porous filter, the pressure drop was plotted against the length of the test, in minutes, and the fouling slope was determined. The lower the slope, the less fouling occurred; the higher the slope, the more fouling occurred. Also, in some of the runs appearing in the following Table, the pressure drop across the filter after 250 minutes of operation is given. In other tests, the number of minutes required to reach a 25-inch mercury pressure differential across the filter is given. A high fouling feed quickly reaches a 25-inch pressure differential while a low fouling feed more slowly reaches this same pressure differential. Finally, in some of the runs set forth in the following table, there is shown the weight, in milligrams, of the deposits collected on the filter after all of the five gallon sample had been run through the test apparatus.

TABLE I.—ERDCO COKER RUNS

Run No.	Feedstock	Additive	Wt. amount, p.p.m.	Fouling slope	250 min. intercept, press., inches Hg.	Minutes required ¹	Weight filter deposit, in mg.
1	(i)	None		High	0.5		1.0
2	(i)	I	80	Low	0.3		1.0
3	(i)	II	35	Very low	0.15		0.5
4	(ii)	III	5	High	5.9		
5	(i)	I	40	Low	0.3		1.0
6	(i)	II	40	Zero	0.15		0.5
7	(i)	Comm. A ²	40	Medium	0.7		0.6
8	Reduced crude	None		High	0.7	5.0	
9	do.	II	40	Medium		15.0	
10	Same as Run 5.	None		do.	1.7		
11	do.	I	25	Low	1.0		
12	do.	II	25	Zero	0.2		
13	Unifiner naphtha	None		High	(³)	23	
14	do.	I	20	Medium	27.0	261	
15	do.	II	20	Low	20	273	
16	(iii)	None		High		22	
17	(iii)	I	40	Medium	13		
18	(iii)	II	40	Very low	5		
19	(iv)	None		Very high	>25.0	177	
20	(iv)	IV	20	Low	0.07		
21	(iv)	Comm. A ²	20	Medium	0.34		
22	(v)	None		High		27	
23	(v)	IV	20	Medium		84	
24	(v)	Comm. A ²	20	High		24	
25	(vi)	None		do.	0.65		
26	(vi)	IV	20	Medium	0.20		
27	(vi)	Comm. A ²	20	Low	0.10		
28	(vii)	None		Medium	0.34		
29	(vii)	IV	10	Low	0.15		
30	(viii)	None		High	0.7		
31	(viii)	IV	15	Medium	0.4		
32	(viii)	IV	25	do.	0.5		
33	(ix)	None		do.	1.3		
34	(ix)	V	25	Very low	0.3		
35	(ix)	VI	25	Low	0.4		

¹ To reach 25-inch Hg press. diff. across filter.² Commercial A: An amide of iso-oleic acid with ethanolamine still bottoms.³ Too high to measure.⁴ Estimated.

NOTE:

I=The amide condensation product of polyisobutyl propionic acid of approximately 800 molecular weight (2.8 moles) with tetraethylenepentamine (1.0 moles). Example 1 product.

II=Same as I plus tris(nonylphenyl)phosphite, 7 parts by weight per part by weight of tri(nonylphenyl) phosphite.

III=Tris(nonylphenyl)phosphite.

IV=Product of Example 2.

V=7 parts [Example 1 product (9 parts) mixed with 1 part copolymer of alkyl methacrylate + N-vinyl pyrrolidone] plus 1 part (tris(nonylphenyl)phosphite).

VI=Same as V except no phosphite ester present.

(i)=A naphtha feed to a catalytic reformer having an API gravity of 57.5; IBP 183° F. and FBP 362° F.

(ii)=A blend of 90% virgin naphtha and 10% steam cracked naphtha having an API of 57.9; IBP 162° F. and FBP 309° F.

(iii)=Visbreaker feedstock, heavy bottoms from vacuum distillation; IBP 700° F. +.

(iv)=Jet fuel (virgin turbo fuel 1 A base, mid-continent crude).

(v)=Heavy catalytic naphtha from fluid cat. cracking, 250° -450° F. cut.

(vi)=Unfinished heating oil (cat. cracked light gas oil).

(vii)=Feedstock to a desulfurizer unit (mixed virgin-cat-coker middle distillate).

(viii)=Crude oil (mid-continent sweet).

(ix)=Another crude oil (mid-continent sour).

From a consideration of the above data, it is apparent that the non-inhibited control feedstocks employed exhibited, for the most part, high fouling slopes when they were subjected to the Erdco Coker Test. These were run without the presence of any additive. On a comparative basis, the use of either a phosphite ester alone or the amine-acid condensation product alone, while in some instances showing an improvement in antifouling tendencies as compared with the control feedstock containing no additives, shows marked improvement in antifouling tendencies when using both the condensation product and the phosphite ester therein. This is particularly true of those feedstocks which are high in olefinic content and is less marked in instances where the feedstock contains considerable quantities of aromatics. Specifically, the following direct comparisons are of significance.

Run 3 with the additive of this invention gives better results (lower 250 min. intercept, lower slope, and lower deposit weight) than do either Run 2 or Run 4 carried out with additives comprising the dispersant and the phosphite ester separately.

Similarly, Run 6 gives better results than Runs 5 or 7, showing our additive to be better than other commercial antifoulant additives. Poor results are shown for the use of the phosphite ester alone (Run 4).

Other data in the table show the combined additives of the invention to comprise a good antifoulant (Test 8 vs. 9) and in general to be better than other antifoulants

(Test 12 vs. 11; 15 vs. 14; 18 vs. 17) in a wide variety of feedstocks.

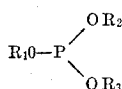
Comparative Runs 19 through 32 represent a series of runs of comparative data involving the use of a reaction product of phosphorous acid with a condensation product of the type described involving the use of five different feedstocks, namely, a jet fuel, a heavy catalytic naphtha, unfinished heating oil, a feedstock to a desulfurizer unit and two types of crude oil. In almost all cases, the comparisons show the superiority of the phosphorous acid reaction product as being superior to either the commercial additive or to the control in which the feedstock was run with no additive present. Outstandingly beneficial results were obtained in Runs 20, 23 and 29. In comparative Runs 33 through 35 involving a crude oil feedstock, extremely beneficial antifoulant results were obtained using the additive (Run 34) comprising an admixture of a polymer, a condensation product, and a phosphite ester. As shown by Run 35 the antifoulant results were not as good as if the phosphite ester was omitted.

Having set forth the general nature and specific embodiments of the invention, what is desired to be secured by Letters Patent is:

1. A method of treating mineral hydrocarbon mixtures employed as feedstocks subjected to elevated temperature of between about 200° and about 1300° F. and which are prone to form deposits which settle out and accumulate on the inner surfaces of heat transfer equipment used in

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processing such feedstocks which comprises heating to said temperatures, said feedstock containing (I) a small amount of the condensation product of an organic monocarboxylic acid, an organic dicarboxylic acid, or an anhydride of either having a number average molecular weight between about 600 and about 5000 and an alkylene polyamine, (II) and a small amount of a phosphite compound having the formula:



wherein R_1 , R_2 and R_3 are each selected from the group consisting of hydrogen, alkyl, chloralkyl, aryl, chloraryl, alkaryl, chloralkaryl, cycloalkyl, chlorcycloalkyl, alkenyl, chloralkenyl, aralkyl, and chloraralkaryl; or the reaction product of (I) with (II).

2. A method as in claim 1 wherein R_1 is a C_1 - C_{50} radical.

3. A method as in claim 1 wherein R_1 , R_2 and R_3 are hydrogen.

4. A method as in claim 1 wherein the combined amount of I and II is between about 1 and about 400 parts per million, by weight, of the feedstock.

5. A method as in claim 4 wherein the weight ratio of I:II is between about 1:1 and about 20:1.

6. A method as in claim 4 wherein I is formed from polyisobutylene of about 780 molecular weight and acrylic acid, and II is tris(nonylphenyl)phosphite.

7. A method as in claim 3 wherein the condensation product is polyisobutylenesuccinic anhydride condensed with tetraethylenepentamine.

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8. A method as in claim 3 wherein the condensation product is polyisobutenylsuccinic anhydride condensed with ethylene dinitrilo tetraethanol.

9. A method as in claim 6 wherein the feedstock is a naphtha containing at least traces of monoolefinic unsaturation.

10. A method as in claim 6 wherein the feedstock is a catalytically cracked petroleum product.

11. A method as in claim 6 wherein the feedstock is a visbreaker feedstock of heavy bottoms from an atmospheric or vacuum distillation.

12. A method as in claim 6 wherein the feedstock is a crude oil.

13. A method as in claim 8 wherein the feedstock is a crude oil.

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