June 25, 1968 R. L. GODAR ET AL 3,390,073

HYDROCARBON ADDITIVE FOR HEAT-EXCHANGER ANTI-FOULING

Filed Sept. 5, 1967 2 Sheets-Sheet 1

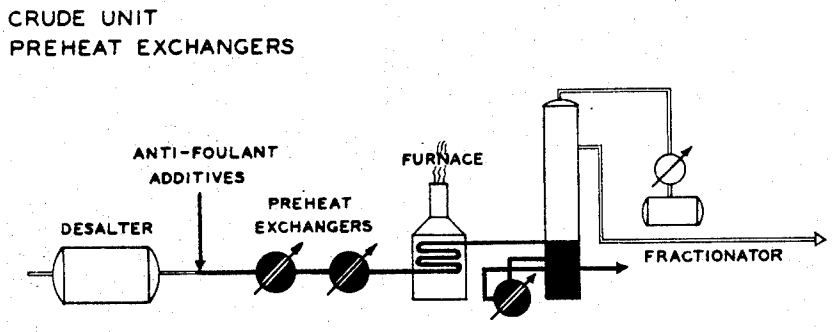


FIG. I

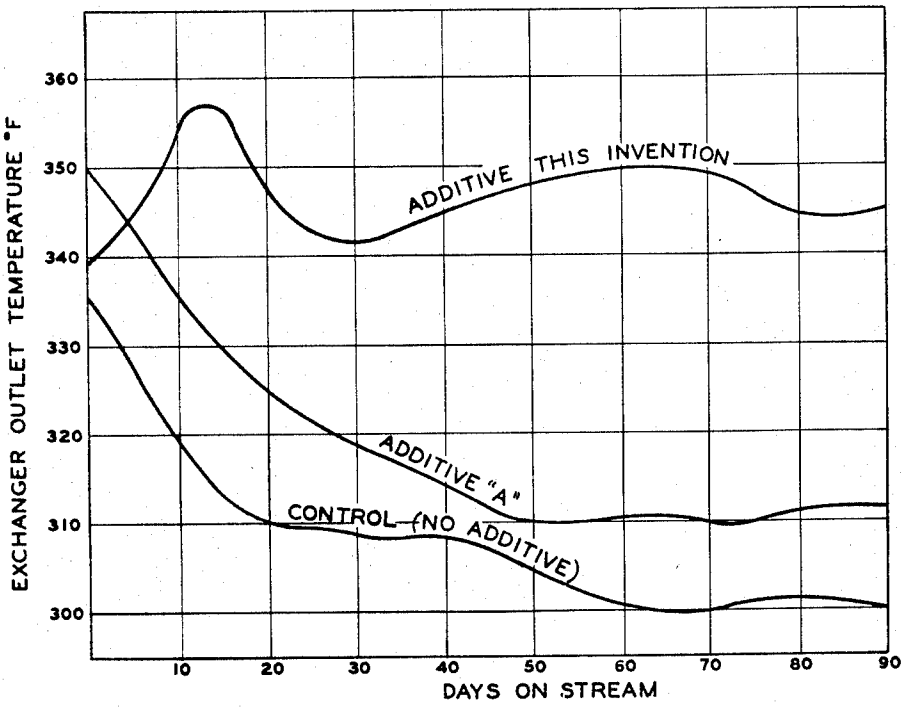


FIG. II

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HYDROCARBON ADDITIVE FOR HEAT-EXCHANGER ANTI-FOULING

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ALKYLATION UNIT
FRACTIONATOR
REBOILERS

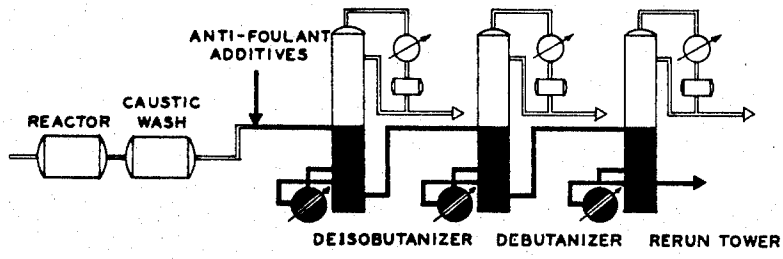


FIG. III

HYDRODESULFURIZATION UNIT
PREHEAT EXCHANGERS

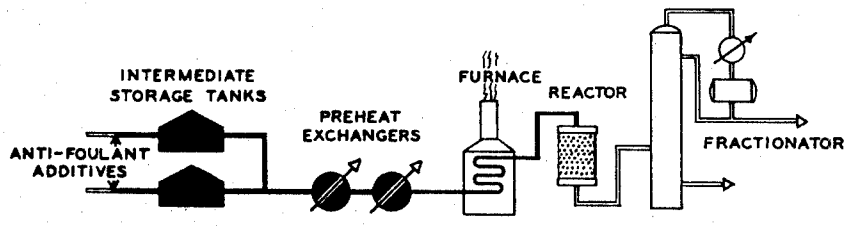


FIG. IV

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HYDROCARBON ADDITIVE FOR HEAT-EXCHANGER ANTI-FOULING

Richard L. Godar, Glendale, Mo., and James L. Richardson, Havertown, Pa., assignors to Petrolite Corporation, a corporation of Delaware

Continuation-in-part of application Ser. No. 380,241, July 6, 1964. This application Sept. 5, 1967, Ser. No. 665,480

4 Claims. (Cl. 208—48)

ABSTRACT OF THE DISCLOSURE

Adhesion of deposits on heat-exchange metal surfaces is inhibited by dosing the hydrocarbon liquid with an antifouling amount of a composition comprising: (1) a secondary amine, (2) a vinylpyrrolidone-acrylic ester copolymer, and (3) optionally, a metal deactivator such as a Schiff base of salicylaldehyde and alkylene diamine.

This application is a continuation-in-part of application Ser. No. 380,241, filed on July 6, 1964, now abandoned.

This invention relates to a method of chemically treating hydrocarbon liquids which contact surfaces under high temperature conditions in order to inhibit, prevent and/or reduce the deposition of substances thereon. More specifically, this invention relates to the chemical treatment of the metal surfaces in contact with petroleum hydrocarbon liquids under conditions of high temperatures whereby said liquids tend to form deposits on such metal surfaces. This invention also relates to compositions employed in these processes.

In the processing of hydrocarbon liquids, particularly petroleum hydrocarbon liquids, elevated temperatures are often used in many necessary and important operations. To handle liquids at elevated temperatures, heat exchangers and the like devices are often employed to control the heat transfer rate from one operational step to another. When hydrocarbon liquids contact hot metal surfaces, there is sometimes a tendency for the liquid to decompose or undergo a chemical reaction that manifests itself in the form of deposits. These deposits may be either coke-like or they may be in the form of tenacious, soft, sticky sludges which adhere to hot surfaces. Adherence of deposits, rather than deposit-formation itself is the essence of the problem, in contrast to fuel storage where residue in the oil itself creates the problem.

The problem is well recognized in the art—note "Petroleum Products Handbook," Guthrie (McGraw-Hill, 1960) pages 1–13, U.S. Patent 2,908,824 and elsewhere.

These deposits tend to materially decrease the heat transfer capacities of the metal surfaces and hence increase operating expenses. These deposits also require additional effort and time to remove and to restore the equipment to its original operating efficiency.

Petroleum refinery operations often encounter the above described conditions in many stages in the refining process. These deposits form on heat transfer surfaces at

temperatures as low as about 200–225° F. and may be evidenced at temperatures as extreme as 800° F.

It is practically impossible to prevent these deposits by coating the metal surfaces with a protective permanent coating due to the possible loss of heat transfer. In addition, the large volume of liquid that contacts such equipment increases the problem of treating metal surfaces in petroleum processing to prevent high temperature deposits.

It would be advantageous if a chemical agent could be added in an extremely small amount to a hydrocarbon liquid which tends to form high temperature deposits whereby such deposits would be prevented. It would also be desirable if such a chemical would not only prevent such deposits but would also remove them without necessitating the stoppage of a given operation. It therefore becomes an object of the present invention to prevent the formation of high temperature deposits on metal surfaces by chemical means.

Another object is to furnish a chemical which when added to a hydrocarbon liquid will prevent the deposit-forming tendencies of said liquid when it contacts metal surfaces at elevated temperatures.

A further object is to provide a chemical treatment which will prevent the formation of high temperature deposits by petroleum hydrocarbon liquids in contact wath heat transfer equipment.

Yet another object is to furnish a chemical treatment capable of being combined with a thermally unstable, deposit-forming liquid whereby said liquid will not form deposits upon metal surfaces at elevated temperatures.

Still another object is to provide a chemical treatment which will remove high temperature deposits from metal surfaces of petroleum refining equipment without the necessity of stopping the operations of such equipment. Other objects will appear hereinafter.

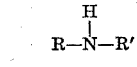
In accomplishing these objects in accordance with the invention it has been found that new and improved results in preventing, inhibiting and/or reducing the formation of deposits from petroleum hydrocarbon liquids during the processing thereof at elevated temperatures, particularly at temperatures within the range of about 200–225° F. to 800° F., are obtained by adding to, preferably by dissolving or dispersing in the hydrocarbon liquid, a secondary amine. Although the secondary amine can be employed alone, its activity is enhanced by one or more of the following oil soluble or dispersible agents:

(1) Acrylic-type polymer and/or copolymers.

(2) A metal deactivator.

The anti-fouling agents employed in this invention are secondary amines. The sum of the carbons on the amine should be sufficient to render the amine soluble in the fuel in the concentrations employed. This solubility property will vary with the particular amine. In general, it is desirable to have the amine contain a total of at least eight carbons, for example, about 10–40 carbons or more, but preferably 12–24 carbons.

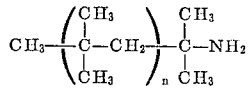
These secondary amines may be symmetrical or unsymmetrical. Thus, amines within the scope of this invention can be described by the general formula



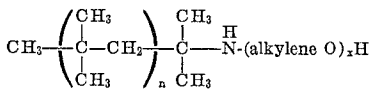
wherein R and R' are aliphatic, cycloaliphatic, aryl, aralkyl, alkaryl, etc., radicals which are preferably hydrocarbon. The R's may also be joined to form a cyclic compound containing nitrogen in the ring. Preferably, the R's are alkyl or cycloalkyl radicals having at least about four carbons on each radical but preferably about 6–12 carbons on each radical.

Provided the secondary amine is soluble in the fuel in the desired concentrations, a wide variety of secondary monoamines can be employed containing one or more of the following radicals: methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, etc. groups. These radicals may be normal or branched, but preferably branched. They may be cycloaliphatic, for example cyclopentyl, cyclohexyl, cycloheptyl, etc. or may contain both alkyl and cycloalkyl radicals, for example octylcyclohexyl amine. In addition, they may contain aromatic groups such as phenyl, naphthyl, benzyl, alkyl phenyl, etc.

The secondary amine may also be substituted. For example, it may contain hydroxy groups. These are readily introduced by oxyalkylation with an α,β-alkylene oxide for example ethylene, propylene, butylene, amylene, styrene, etc. oxides. For example, a monoamine may be oxyalkylated with an alkylene oxide to yield a secondary amine. Thus, a Primene



may be oxyalkylated to yield



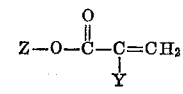
where x is 1 or more such as about 1–25 or more but preferably 1–5 and where n=0–5.

Oxyalkylation is readily controlled with a "Primene" to form a secondary amine since only one nitrogen-bonded hydrogen is reactive.

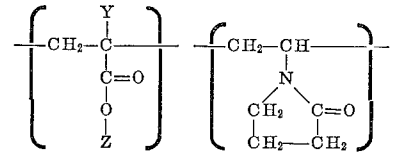
In summary, any secondary amine which is oil soluble at use concentration can be employed. The radicals of the amine may be aliphatic, cycloaliphatic, heterocyclic, aryl, alkaryl, alkanol, aralkyl, substituted derivatives of the above, etc. In addition the amine may contain more than one of the above radicals. In general, it is desirable that the amine contain a total of at least 8 carbons, such as 8–40 carbons, but preferably 12–24 carbons.

In addition to the secondary amine, other auxiliary additives may also be employed to enhance the antifoulant function of the secondary amine.

One auxiliary additive is a copolymer derived from an acrylic ester of the formula:



and N-vinyl-2-pyrrolidone, for example a copolymer containing the following units:



having a molecular weight for example of at least 50,000, for example 50,000–500,000, or higher, but preferably 100,000–400,000 with an optimum of 300,000–400,000 of which vinyl pyrrolidone comprises at least 1% by weight of the copolymer, for example 1–30%, but preferably 3–15% with an optimum of 5–10%; where Y is hydrogen, a lower alkyl group such as methyl, ethyl, etc., Z is an hydrocarbon group having, for example, 1–30 carbon atoms, but preferably 8–18 carbon atoms. These polymers are preferably acrylic or methacrylic polymers or polymers derived from both in conjunction with vinyl pyrrolidone. The Z group on the polymer, which can be the same throughout or mixed, can be octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, octadecyl, etc. Lower alkyl groups can also be employed such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, etc., but they preferably are employed as copolymers of the higher Z groups, for example a copolymer of dodecyl methacrylate and methyl acrylate, etc. The acrylic ester units may be derived from one or more acrylic type monomers and may be fully acrylic or fully methacrylic or both acrylic and methacrylic. The polymer may be random, block graft, etc.

Also, Z may also be an alkylated aromatic group such as butyl phenyl, amyl phenyl, etc., or a cycloaliphatic group such as cyclohexyl. Thus, non-limiting specific examples of suitable monomeric esters are: methyl acrylate, ethyl acrylate, propyl methacrylate, amyl acrylate, lauryl acrylate, cetyl acrylate, octadecyl acrylate, amyl methacrylate, lauryl methacrylate, cetyl methacrylate, octadecyl methacrylate, amylphenyl methacrylate, cyclohexyl methacrylate, etc., including the analogous acylate or methacrylate esters. Copolymers of the above and other acrylic esters may be used, for example, a copolymer of methyl or ethyl acrylate and dodecyl methacrylate in conjunction with vinyl pyrrolidone. However, it should be understood that this description does not preclude the presence of small amounts of unesterfied groups being present in the polymer, i.e. approximately 5% or less of where Z=H.

It should be understood, of course, that when the above compounds are polymerized, the polymerization should not be carried to such an extent as to form polymers which are insoluble or non-dispersible in the petroleum hydrocarbon used. The polymerization may be carried out by methods known to the art, such as by heating mildly in the presence of a small amount of benzoyl peroxide, but the method of polymerization is not part of this invention. For examples of acrylic-vinyl pyrrolidone copolymers see French Patent 1,163,033.

The following are some illustrative examples of vinyl pyrrolidone-acrylic ester type resins which can be employed in this invention.

TABLE I.—VINYL PYRROLIDONE-ACRYLIC ESTER-TYPE RESINS

Ex.	Monomer 1	Monomer 2	Monomer 3	Vinyl Pyrrolidone, percent by wt.	Mol Ratio 1:2:3	Avg. Mol Weight
1	Tridecyl Methacrylate	Octadecyl Methacrylate		7.5	1:1	300,000
2	Dodecyl Methacrylate			10		500,000
3	do	Butyl Acrylate		15	2:1	400,000
4	Octadecyl Methacrylate			5		450,000
5	Tridecyl Methacrylate			20		350,000
6	Octadecyl Methacrylate	Methyl Methacrylate		10	3:1	500,000
7	Dodecyl Methacrylate	Ethyl Acrylate		5	4:1	400,000
8	Cetyl Methacrylate	Octadecyl Methacrylate	Butyl Methacrylate	7.5	2:1:0.5	350,000

Another illustrative example of a vinyl pyrrolidone-acrylic ester type resin, hereinafter referred to as Additive VPA, which can be employed in this invention, is prepared by polymerizing 65 parts by weight of an alkyl methacrylate, where the alkyl portion is obtained from a commercial cut of C_{12} to C_{18} fatty alcohols, 25 parts by weight of butyl methacrylate, and 10 parts by weight of N-vinyl pyrrolidone. In making this ester type resin by polymerization 0.075 part, by weight of the monomer mixture, of benzoyl peroxide is added to said mixture, and the so-formed mixture is stirred and warmed to dissolve the benzoyl peroxide. Then, 20 parts, by weight of said mixture, of a white mineral oil is added to a reaction vessel which is swept out with nitrogen gas, and the so-formed mixture is slowly added to said white mineral oil in said reaction vessel over a two hour period. At 2.6 hours, 0.015 part, by weight of said monomer mixture, of benzoyl peroxide is added to the vessel. Then, at 4, 4.6, 5.3 and 6 hours, respectively, further additions of 0.022 part, by weight of said monomer mixture, are made and during this time and until 9–10 hours, when heating is discontinued, temperatures are maintained between 97° C. and 103° C. At 6.5 hours, 28 parts of white mineral oil are added, and the batch is stripped of volatile products by being heated up to 145° C. at 2 mm. pressure, giving a yield of about 90% of copolymer having an average molecular weight of 450,000.

Another auxiliary additive is a metal deactivator, for example, those conveniently employed in deactivating copper, iron and other metals from hydrocarbon systems. Typical examples are those described in U.S. Patent 2,282,513. Of course, one skilled in the art is aware that many other metal deactivators are known and can be employed herein.

The compounds employed as metal deactivators are preferably of the type of Schiff's bases and may be represented by the formulae

(1) A—CH=N—R—N=CH—B

and preferably,

(2) HO—A—CH=N—R—N=CH—B—OH

wherein A and B each represents an organic radical and preferably a hydrocarbon radical. In Formula (1) A and B each preferably represents a hydrocarbon radical. In Formula (2) A and B each preferably represents an aromatic ring or an unsaturated heterocyclic ring in which the hydroxyl radical is attached directly to a ring carbon atom ortho to the —CH=N group. R represents an aliphatic radical having the two N atoms attached directly to different carbon atoms of the same open chain. The preferred metal deactivator is that formed from salicylaldehyde and 1,3-propylenediamine.

Typical examples of aldehyde and polyamines employed in preparing these Schiff bases include the following:

Aldehydes

Benzaldehyde
2-methylbenzaldehyde
3-methylbenzaldehyde
4-methylbenzaldehyde
2-methoxybenzaldehyde
4-methoxybenzaldehyde
a-Naphthaldehyde
b-Naphthaldehyde
4-phenylbenzaldehyde
Propionaldehyde
n-Butyraldheyde
Heptaldehyde
Aldol
2-hydroxybenzaldehyde
2-hydroxy-6-methylbenzaldehyde
2-hydroxy-3-methoxybenzaldehyde
2-4-dihydroxybenzaldehyde
2-6-dihydroxybenzaldehyde
2-hydroxynaphthaldehyde-1
1-hydroxynaphthaldehyde-2
Anthrol-2-aldehyde-1
2-hydroxyfluorene-aldehyde-1
4-hydroxydiphenyl-aldehyde-3
3-hydroxyphenanthrene-aldehyde-4
1-3-dihydroxy-2-4-dialdehyde-benzene
2-hydroxy-5-chlorobenzaldehyde
2-hydroxy-3-5-dibromobenzaldehyde
2-hydroxy-3-nitrobenzaldehyde
2-hydroxy-3-cyanobenzaldehyde
2-hydroxy-3-carboxybenzaldehyde
4-hydroxypyridine-aldehyde-3
4-hydroxyquinoline-aldehyde-3
7-hydroxyquinoline-aldehyde-8

Polyamines

Ethylenediamine
1-2-propylenediamine
1-3-propylenediamine
1-6-hexamethylenediamine
1-10-decamethylenediamine
Diethylenetriamine
Triethylenetetramine
Pentaerythrityltetramine
1-2-diaminocyclohexane
Di-(b-aminoethyl) ether
Di-(b-aminoethyl) sulfide

Where auxiliary additives are employed, the ratio of these additives to the secondary amine can also vary widely. In general the weight ratio of secondary amine to the acrylic-type polymer is at least 1:1, from about 1:1 to 100:1 such as about 2:1 to 50:1, for example, from about 3:1 to 20:1 but preferably from about 5:1 to 15:1.

In general, the ratio of secondary amines to metal deactivators is at least about 1:1, from about 1:1 to 100:1 such as about 2:1 to 50:1, for example from about 3:1 to 20:1 but preferably about 5:1 to 15:1.

The following examples are presented by way of illustration and not of limitation.

EXAMPLE 1

The antifoulants of this invention are employed in a crude unit preheat exchanger of the type shown in FIGURE 1.

A refinery in Eastern United States had, for a number of years, encountered fouling on the crude side of its crude unit preheat exchanger following the desalter.

The crude is preheated and desalted. The desalted crude is picked up with a hot oil pump and passed through a gas oil exchanger, into an inter-reflux exchanger, through a wax exchanger, and then into a vacuum bottoms exchanger. The crude then enters the furnace.

Operational data

Thru-put	b.d.p.	11,500
Type crude		Penna. grade
A.P.I. gravity		39° to 44°
Raw crude salt content	p.t.b.	2 to 10
Raw crude sediment	p.t.b.	20
Desalted crude salt content	p.t.b.	0 to 2
Desalted crude sediment	p.t.b.	Trace to 2

Without antifoulants the length of crude runs before shutdown for cleaning the heat exchanger was approximately 2½ to 3 months. During this period there would be a reduction of heat in the crude unit preheat exchangers which would result in a 50° F. loss of temperature at the furnace inlet. This would cause a reduction in thru-put because the furnace operated at maximum capacity when the exchangers were clean. The average reduction of charge during this period was about 1,000 b.p.d.

Over a period of time several different approaches and additives were tried to correct the problem. Commercial additive "A" was beneficial but costly. Instead of a 50° F. drop in crude unit preheat in the 2½ to 3 months it was found that one could control it to a 30 to 35° F. loss and the loss was not so rapid. Commercial additive "B" was plant tested and found to have very little, if any, effect upon retarding fouling. An antifoulant additive of this invention was injected into the suction of the hot oil pump following the desalter at 4.36 p.p.m. based on weight of the crude charge rate. The result of this run and those with additives "A" and "B" are as follows:

EXCHANGE OUTLET TEMPERATURE, ° F.

Days on Stream	Additive "A"	Additive "B"	Additive of Invention [1]
2	345	329	340
10	336	315	354
20	324	317	345
30	317	305	345
40	313	[2] 304	347
50	312		352
60	314		347
70	[2] 309		353
80			342
90			343

[1] Dicyclohexylamine 4 ppm and Additive VPA 0.36 p.p.m., based on weight of crude.
[2] Shutdown for cleaning heat exchanger.

The results of this example are also shown in Figure II which is a graph plotting Exchange Outlet Temperature (EF.) vs. Days on Stream which compares the crude having no additive (control), the crude containing the best of the competing commercial additives (Additive "A") and the crude containing the additive of this invention.

These examples clearly illustrate the effectiveness of the additives of the invention.

EXAMPLE 2

The antifoulants of this invention are also employed in alkylation unit fractionation reboilers of the type shown in Figure III.

Alkylation reactions and subsequent caustic neutralization often produce small quantities of undesirable side products such as sodium salts and high-molecular-weight polymers. Because of the high vaporization rates in the reboilers following the fractionators, much of this material is trapped in the system. The reboiler fouling which results often prevents the maintenance of adequate tower bottom temperatures. The injection of 4–10 p.p.m. of the anti-fouling additive of this invention prevents the formation of an insulating layer on the reboiler tubes. In cases where fouling occurs throughout the fractionation system, the additive can be injected at 10 p.p.m. into the charge to the first tower in the series. Because the additive is not volatile at these temperatures, it will migrate from tower to tower, thus keeping the entire fractionation system clean.

EXAMPLE 3

The antifoulants of this invention are also employed in the hydrosulfurization unit preheat exchanges of the type shown in Figure IV.

Severe process stream fouling frequently occurs in processing where straight run and catalytic-cracked stocks are blended prior to desulfurizing. During intermediate storage small quantities of oxygen may be absorbed, promoting polymerizaiton reactions as the combined streams are heated to desulfurization temperatures. The injection of 4 to 10 p.p.m. of the antifoulant of this invention reduces polymer formation and prevents deposition on exchanger tubes.

In addition the additives of this invention can be employed in other systems known to the petroleum art.

The following additives also may be successfully employed as antifoulants:

	Wt. ratio
Di-n-heptylamine:	
Di-n-heptylamine+additive VPA	49:1
Do	99:1
Do	9:1
Do	4:1
Di-myristylamine:	
Di-myristylamine+additive VPA	4:1
Do	99:1
Do	19:1
Di-2-ethylhexylamine:	
Di-2-ethylhexylamine+additive VPA	9:1
Dilaurylamine:	
Dilaurylamine+additive VPA	49:1
Do	99:1
Armeen 2HT (di-hydrogenated tallow amine):	
Armeen 2HT+additive VPA	99:1
Dibenzylamine:	
Dibenzylamine+additive VPA	9:1
Do	99:1
$RNHCH_2CH_2CH_2CH_2OH$ (R=Primene (12–14 carbons), 81R:	
$RNHCH_2CH_2CH_2CH_2CH_2OH$+additive VPA	49:1
$RNHCH_2CH_2CH_2CH_2OH$+additive VPA	99:1

The antifouling additive system of this invention can be employed in refining crude petroleum as well as in the treatment of any component thereof which are exposed to high temperatures including the light distillates, for example light naphthas, intermediate naphthas, heavy naphthas, etc.; middle distillates, for example kerosene, gas oil, etc.; distillate lube oil stocks, for example, white oil, saturating oil, light lube oil, medium lube oil, heavy lube oil, and the like.

In addition, the additive can be employed with other hydrocarbons such as xylene, benzene, purified hydrocarbon compounds, etc. In addition, they can be employed under certain conditions with non-hydrocarbons, such as alcohols, phenols, etc. For example, they can be employed in a toluene extraction tower and stripper which process comprises mixing phenol and toluene in an extraction whereby phenol extracts impurities from toluene and the raffinate is subsequently removed. Thereafter the mixture is sent to a stripper where the toluene is removed from the phenol by distillation. The remaining phenol is recycled to the extractor for further use. The system is operated over a wide temperature range, for example 230–425° F. Deposits in the phenol circuit cause the loss of excessive amounts of phenol. It can be used in heat transfer units used in a furfurol extraction process, processing for example, intermediate distillates, paraffin distillates, decanted oil, vacuum cylinder stock, deasphalted cylinder stock, etc.

The amount of antifouling agent required in this invention is subject to wide variation but in general very effective results have been obtained by adding relatively minute amounts of the antifouling agent to the hydrocarbon liquid being processed, for example, amounts may be as low as 0.5 p.p.m. in hydrocarbon liquid, for example 1 to 500 p.p.m. or higher, for example 1000 or more p.p.m., preferably 1 to 100 p.p.m., with an optimum of 3–30 p.p.m. In general, the upper limit is determined by

the economics of the process but other factors should be taken into consideration, such as whether large amounts will have any adverse effects on present or subsequent operations. Because of the many different types of operations where hydrocarbons are heated to elevated temperatures under conditions where deposits are formed, it is difficult to give specific ranges which will be effective in all operations. The amount of agent which inhibits the formation of deposits is referred to herein as an "antifouling amount." The above figures relate to p.p.m. in terms of active antifouling chemical not including the solvent employed.

Inasmuch as the antifouling agent is employed in such small amounts and it is preferable to feed them continuously or semi-continuously by means of a proportioning pump or other suitable device to the particular hydrocarbon liquid being processed or to add them in a similar manner to the apparatus in which the hydrocarbon liquid is being processed, it is desirable to incorporate the agent or a mixture of agents into a suitable solvent which will be compatible with the liquid which is to be processed. The solvent which is used to dissolve the active ingredient is also subject to some variation depending upon the solubility characteristics of the particular compound employed. In some cases, even though the active mixture is insoluble in a particular solvent, it will dissolve in a combination of solvents.

In the practice of the invention it is very desirable to start the treatment with the chemicals employed for the purpose of the invention at a higher dosage and then gradually reduce the dosage to the point where fouling of the apparatus is just eliminated.

The invention is especially valuable where sour naphthas are being processed or where the oil being processed is a mixture containing some sour naphthas.

Examples of specific types of apparatus to which the chemical compositions of the invention can be added during petroleum processing are fractioning towers, stripping columns, debutanizers, depropanizers, deethanizers, heat exchangers, reboilers, hot product lines and other metal equipment (usually ferrous metal) which is brought into contact with the organic liquids being processed at relatively high temperatures. The invention makes it possible to extend the useful life of crude oil fractionating towers and other types of petroleum refinery equipment. It also makes it possible to provide cleaner inside surfaces resulting in better fractionation, better heat exchange in coolers, far less severe plugging and less time required for cleaning and maintenance.

This invention also relates to improved fuel oil compositions. More particularly, it is concerned with the provision of fuel oils which have been stabilized against the formation of color and sediment therein during storage.

Fuel oils in general are contemplated by the invention. The fuel oils with which this invention is especially concerned are hydrocarbon fractions having an initial boiling point of at least about 100° F. and an end point not higher than about 750° F., and boiling substantially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It will be understood, however, that this term is not restricted to straight-run distillate fractions. Thus, as is well known to those skilled in the art, the distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillates, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as acid or caustic treatment, solvent refining, clay treatment, etc.

The distillate fuel oils are characterized by their relatively low viscosities, pour points, and the like. The principal property which characterizes the contemplated hydrocarbon fractions, however, is the distillation range. As mentioned hereinbefore, this range will lie between about 100° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Especially contemplated herein are Nos. 1, 2 and 3 fuel oils used in domestic heating and as diesel fuel oils, particularly those made up chiefly or entirely of cracked distillate stocks. The domestic heating oils generally conform to the specifications set forth in A.S.T.M. Specifications D396–48T. Specifications for diesel fuels are defined in A.S.T.M. Specifications D975–48T. Also contemplated herein are fuels for jet combustion engines. Typical jet fuels are defined in Military Specification MIL–F–5624B.

As is well known, fuel oils have a tendency to deteriorate in storage and form colored bodies and sludge therein. This deterioration of the oil is highly undesirable in that it causes serious adverse effects on the characteristics of the oil, particularly on the ignition and burning qualities thereof. It is also a contributory factor, along with the presence of other impurities in the oil, such as rust, dirt and moisture, in causing clogging of the equipment parts, such as screens, filters, nozzles, etc., as is explained further hereinbelow. An important economical factor is also involved in the problem of oil deterioration in storage, viz., customer resistance. Thus, customers judge the quality of an oil by its color and they oftentimes refuse to purchase highly colored oils. It will be appreciated then that since fuel oils of necessity are generally subject to considerable periods of storage prior to use, the provision of a practical means for preventing the deterioration of the fuel oil during such storage would be a highly desirable and important contribution to the art. It is the principal object of the present invention to provide such means. Other and further objects will be apparent from the following description of the invention.

In accordance with the present invention, it has now been found that oil deterioration in storage, with attendant formation of color and sludge in the oil, can be successfully inhibited by the addition to the oil of a small amount of a secondary amine in conjunction with an acrylic type polymer and in certain instances with a metal deactivator. The concentrations and ratios employed for this use are the same as those employed in the antifoulant application.

The compositions of this invention containing both (1) the secondary amine and (2) the acrylic-type polymer, and in certain instances (3) a metal deactivator have been found to improve the color stability and resistance to sedimentation of fuel oils. The effect of the combination of (1) and (2) is greater than that effected by either (1) or (2) alone. With certain fuels (3) further improves the fuel.

The following specific examples are presented for purposes of illustrating the fuel oil compositions of this invention. It is to be understood that this invention is not to be limited by the particular additives and fuel oils. Other additives, as discussed herein, are utilizable, as those skilled in the art will readily realize.

The test used to determine the sedimentation characteristic of the fuel oils is the 110° F. storage test where a 500 ml. sample of fuel oil under test is placed in a convected oven maintained at 110° F. for a period of six weeks, then the sample is removed from the oven and cooled. The cooled sample is filtered through a tarred asbestos filter (Gooch Crucible) to remove insoluble matter. The weight of such matter, in mgs., is reported as the amount of sediment. In the test a sample of the blank uninhibited oil is run along with the fuel oil blend under test. The effectiveness of the fuel compositions is determined by comparing the test data therefrom with the test data for the uninhibited blank fuel oil.

The results are presented in the following tables.

TABLE II.—#2 FUEL OIL A

[Cycle oil/kerosine/coker distillate (60:30:10) After 6 weeks' storage at 110° F.]

Additive	Mg. residue/100 ml. sample at 15 p.p.m.	Mg. residue/100 ml. sample at 30 p.p.m.
None (4.4 mg./100 ml.)		
Additive VPA	3.6	5.0
Dicyclohexylamine		0.8
Additive VPA+Dicyclohexylamine (1:9)		0.5
Di-n-heptylamine	1.3	0.6
Di-n-heptylamine+Additive VPA (49:1)	1.1	
Di-n-heptylamine+Additive VPA (99:1)		
Di-n-heptylamine+Additive VPA (9:1)	1.0	
Di-n-heptylamine+Additive VPA (4:1)	0.7	
Alamine 205 (Dimyristyl amine—Gen. Mills)	1.1	1.0
Alamine 205+Additive VPA (4:1)	0.9	
Alamine 205+Additive VPA (99:1)		0.7
Alamine 205+Additive VPA (19:1)		0.7
Di-2-ethylhexylamine		0.9
Di-2-ethylhexylamine+Additive VPA (9:1)		0.6
Alamine 204 (Dilauryl amine—Gen. Mills)	0.8	0.7
Alamine 204+Additive VPA (49:1)	0.6	
Alamine 204+Additive VPA (99:1)		0.5
Armeen 2HT (Dihydrogenated tallow amine (Armour))		0.9
Armeen 2HT+Additive VPA (99:1)		0.6
Dibenzylamine	1.3	1.0
Dibenzylamine+Additive VPA (9:1)	1.1	
Dibenzylamine+Additive VPA (99:1)		0.8
$RNHCH_2CH_2CH_2CH_2OH$*	0.7	0.6
$RNHCH_2CN_2CN_2CN_2OH$*+ Additive VPA (49:1)	0.5	
$RNHCH_2CH_2CH_2CH_2OH$*+ Additive VPA (19:1)		0.3

*Where R is a mixture of isomers having 12–14 carbon atoms, with tertiary alkyl structure, i.e., this amine is monooxybutylated Primene 81R.

TABLE III.—#2 FUEL OIL B

[Cycl e oil/kerosine/coker distillate (30:65:5) After 6 weeks' storage at 110° F.]

Additive	Mg. residue/100 ml. sample at 7.5 p.p.m.	Mg. residue/100 ml. sample at 15 p.p.m.	Mg. residue/100 ml. sample at 30 p.p.m.
None (1.9 mg./100 ml.)			
Additive VPA	1.9	1.8	1.7
Di-n-butylamine		1.1	0.7
Di-n-butylamine + Additive VPA (99:1)			0.5
Di-n-butylamine + Additive VPA (49:1)		0.8	
Di-n-amylamine			0.9
Di-n-amylamine + Additive VPA (9:1)			0.6
Dicyclohexylamine	1.1	0.9	0.6
Dicyclohexylamine + Additive VPA (24:1)	0.9		
Dicyclohexylamine + Additive VPA (49:1)		0.7	
Dicyclohexylamine + Additive VPA (9:1)		0.7	
Dicyclohexylamine + Additive VPA (3:2)	0.6		
Dicyclohexylamine + Additive VPA (4:1)		0.6	
Dicyclohexylamine + Additive VPA (9:1)			0.5
Di-n-heptylamine		1.1	
Di-n-heptylamine + Additive VPA (4:1)		0.6	
Di-n-octylamine		1.1	0.9
Di-n-octylamine + Additive VPA (49:1)		0.9	
Di-n-octylamine + Additive VPA (9:1)		0.9	
Di-n-octylamine + Additive VPA (4:1)		0.9	
Di-n-octylamine + Additive VPA (9:1)			0.7
Alamine 205			1.1
Alamine 205 + Additive VPA (99:1)			0.9
Di-2-ethylhexylamine	1.8		
Di-2-ethylhexylamine + Additive VPA (3:2)	1.5		
Monooxybutylated Primene	1.3	1.2	1.1
Monooxybutylated Primene + Additive VPA (4:1)	1.1	0.9	
Monooxybutylated Primene +Additive VPA (9:1)		0.9	0.8
Monooxybutylated Primene + Additive VPA (99:1)			0.8

Although the present invention has been described in conjunction with preferred embodiments, it will be understood that modifications and variations may be resorted to without departing from the spirit and scope of this invention. Such variations and modifications are considered to be within the scope and purview of the appended claims.

Having thus described our invention what we claim as new and desire to obtain Letters Patent is:

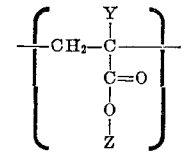
1. A process for inhibiting in oil refining apparatus during petroleum refining operations the formation of adherent coke-like deposits and adherent tenacious soft, sticky sludges on, and the adhesion of said deposits and said sludges to, the hot metal heat transfer surfaces of a heat exchanger in said oil refining apparatus by a thermally unstable petroleum hydrocarbon liquid, said petroleum hydrocarbon liquid having the tendency to undergo a chemical reaction at a temperature in the range of about 200° F. to 800° F., said chemical reaction manifesting itself in the form of adherent coke-like deposits and adherent soft, sticky sludges, such as are usually formed during passage of said petroleum hydrocarbon liquid through said heat exchanger and in contact with the hot metal surfaces of said heat exchanger in said oil refining apparatus at a temperature in the range of about 200° F. to 800° F. comprising

(1) incorporating in said petroleum hydrocarbon liquid prior to contact with said metal surfaces of said heat exchanger in said oil refining apparatus an antifouling amount of a composition comprising

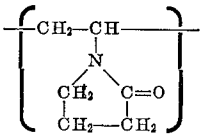
(A) a petroleum hydrocarbon liquid soluble secondary amine and

(B) a copolymer containing the units

(a)



(b)



and having a molecular weight of 50,000–500,000, unit (b) being at least 1–30% by weight of the copolymer, Y being selected from the group consisting of hydrogen and a lower alkyl group and Z being a hydrocarbon group having 1–30 carbon atoms.

the weight ratio of A and B being from about 1:1 to 100:1, and

(2) heating said petroleum hydrocarbon liquid having incorporated therein said composition in an antifouling amount to a temperature in the range of about 200° F. to 800° F. by contact with said hot

metal surfaces of said heat exchanger in said oil refining apparatus.

2. The process of claim 1 wherein the secondary amine is dicyclohexyl amine.

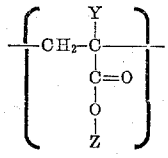
3. A process for inhibiting in oil refining apparatus during petroleum refining operations the formation of adherent coke-like deposits and adherent tenacious soft, sticky sludges on, and the adhesion of said deposits and said sludges to, the hot metal heat transfer surfaces of a heat exchanger in said oil refining apparatus by a thermally unstable petroleum hydrocarbon liquid, said petroleum hydrocarbon liquid having the tendency to undergo a chemical reaction at a temperature in the range of about 200° F. to 800° F., said chemical reaction manifesting itself in the form of adherent coke-like deposits and adherent soft, sticky sludges, such as are usually formed during passage of said petroleum hydrocarbon liquid through said heat exchanger and in contact with the hot metal surfaces of said heat exchanger in said oil refining apparatus at a temperature in the range of about 200° F. to 800° F. comprising

(1) incorporating in said petroleum hydrocarbon liquid prior to contact with said metal surfaces of said heat exchanger in said oil refining apparatus an antifouling amount of a composition comprising

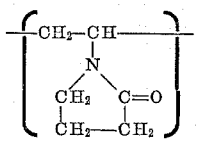
(A) a petroleum hydrocarbon liquid soluble secondary amine,

(B) a copolymer containing the units

(a)



(b)



and having a molecular weight of 50,000–500,000, unit (b) being at least 1–30% by weight of the copolymer, Y being selected from the group consisting of hydrogen and a lower alkyl group, and Z being a hydrocarbon group having 1–30 carbon atoms, and

(C) a metal deactivator,

the weight ratio of A to B being from about 1:1 to 100:1 and the weight ratio of A to C being from about 1:1 to 100:1, and

(2) heating said petroleum hydrocarbon liquid having incorportaed therein said composition in an antifouling amount to a temperature in the range of about 200° F. to 800° F. by contact with said hot metal surfaces of said heat exchanger in said oil refining apparatus.

4. The process of claim 3 wherein the secondary amine is dicyclohexyl amine and the metal deactivator is a Schiff base formed from salicyladehyde and an alkylene polyamine.

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