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PROCESS OF INHIBITING DEPOSITION OF ORGANIC SUBSTANCES IN HEAT EXCHANGERS AND THE LIKE OPERATING AT ELEVATED TEMPERATURES

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The present invention relates to a method of chemically treating hydrocarbon liquids contacting metal surfaces under high temperature conditions to prevent the deposition of organic substances thereon. More specifically it 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.

In the processing of hydrocarbon liquids, particularly petroleum hydrocarbon liquids, elevated temperatures are often used in many necessary and important production operations. To handle liquids at elevated temperatures heat exchangers and 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. In the first instance, the deposits may be considered as pyrolyzed decomposition products whereas in the second type they may be considered as oxidation products and/or polymerizate compositions.

In either of the above cases the deposits tend to materially decrease the heat treansfer 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 225° F. and may be evidenced at temperatures as extreme as 800° F.

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

It would be advantageous if a chemical treatment 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 carbonaceous 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 with 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 carbonaceous 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 inhibiting the formation of organic deposits from petroleum hydrocarbon liquids during the processing thereof at elevated temperatures, particularly at temperatures within the range of about 225° F. to 800° F., are obtained by adding, preferably by dissolving in the hydrocarbon liquid, a salt of an organic aliphatic dicarboxylic acid containing at least 10 carbon atoms in a hydrocarbon structure and a glyoxalidine wherein the carbon atom in the 2-position is linked to a higher aliphatic hydrocarbon group containing at least 8 carbon atoms, the carbon atom in the 4-position is linked to a member from the group consisting of hydrogen and lower aliphatic hydrocarbon groups containing not more than 6 carbon atoms, the carbon atom in the 5-position is linked to a member from the group consisting of hydrogen and lower aliphatic hydrocarbon groups containing not more than 6 carbon atoms, there being at least one hydrogen atom on each of the carbon atoms in the 4- and 5-positions, and the nitrogen atom in the 1-position is linked to a member from the group consisting of hydrogen and lower aliphatic groups containing not more than 6 carbon atoms, said last named lower aliphatic groups being composed of atoms from the group consisting of hydrogen, carbon, nitrogen and oxygen.

These compounds can also be characterized as monoglyoxalidine salts of said organic aliphatic dicarboxylic acids or diglyoxalidine salts of such acids, depending upon whether one or two mols of the glyoxalidine is reacted with the organic aliphatic dicarboxylic acid. If only one mol of the plyoxalidine is reacted the resultant compound is a monoamine salt containing a free carboxylic acid group. If two mols of the glyoxalidine are reacted the resultant compound is a diamine salt. The glyoxalidines employed as starting materials are made by well known procedures by reacting a fatty acid with an aliphatic polyamine with the elimination of water as described, for example, in Wilson, U.S. Patent 2,267,965 and Wilkes et al. U.S. Patent 2,268,273.

The glyoxalidines with which the present invention is particularly concerned are those in which the glyoxalidine portion of the molecule is derived by reacting together one of the acids from the group consisting of lauric acid, myristic acid, palmitic acid, oleic acid and stearic acid, with an aliphatic polyamine from the group consisting of aminoethylethanolamine, diethylenetriamine and triethylene tetramine. When the glyoxalidine is derived from aminoethylethanolamine the resultant product contains a hydroxyethyl group on the 1-position. When the glyoxalidine is derived from diethylenetriamine the resultant product contains an aminoethyl group in the 1-position, and when the glyoxalidine is derived from triethylenetetramine the resultant product contains a (2-aminoethyl-aminoethyl group in the 1-position.

The number of carbon atoms in the aliphatic hydrocarbon group in the 2-position is always one less than that in the aliphatic carboxylic acid from which the glyoxalidine is derived. Thus, if the glyoxalidine is made from lauric acid the hydrocarbon group in the 2-position

will contain 11 carbon atoms. If the glyoxalidine is made from oleic acid the hydrocarbon group in the 2-position will be a heptadecenyl group containing 17 carbon atoms. The hydrocarbon group in the 2-position preferably contains 13 to 17 carbon atoms for the purpose of the present invention.

Specific examples of glyoxalidines that can be reacted with sebacic acid, dilinoleic acid and other long chain organic aliphatic dicarboxylic acids in preparing salts suitable for the purpose of the invention are: 1-(2-hydroxyethyl)-2-undecyl glyoxalidine, 1-(2-hydroxyethyl)-2-tridecyl glyoxalidine, 1-(2-hydroxyethyl)-2-pentadecyl glyoxalidine, 1-(2-hydroxyethyl)-2-heptadecyl glyoxalidine, 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine, 1-(2-aminoethyl)-2-undecyl glyoxalidine, 1-(2-aminoethyl)-2-tridecyl glyoxalidine, 1-(2-aminoethyl)-2-pentadecyl glyoxalidine, 1-(2-aminoethyl)-2-heptadecyl glyoxalidine, 1-(2-aminoethyl)-2-heptadecenyl glyoxalidine, 1-[(2-aminoethyl)-aminoethyl]-2-undecyl glyoxalidine, 1-[(2-aminoethyl)-aminoethyl]-2-tridecyl glyoxalidine, 1-[(2-aminoethyl)-aminoethyl]-2-pentadecyl glyoxalidine, 1-[(2-aminoethyl)-aminoethyl]-2-heptadecyl glyoxalidine, 1-[(2-aminoethyl-aminoethyl]-2-heptadecenyl glyoxalidine, 4-methyl-2-undecyl glyoxalidine, 4-methyl-2-tridecyl glyoxalidine, 4-methyl-2-pentadecyl glyoxalidine, 4-methyl-2-heptadecyl glyoxalidine, 4-methyl-2-heptadecenyl glyoxalidine.

The organic aliphatic dicarboxylic acid salts are prepared by mixing a glyoxalidine of the types described and an organic aliphatic dicarboxylic acid of the type described in mol ratios of 1:1 in case it is desired to prepare the monoamine salt, or 2:1 in case it is desired to prepare the diamine salt, and warming the reaction mixture at temperatures sufficient to melt the dicarboxylic acid if it is a solid for 5 to 15 minutes with or without a catalyst until homogeneous materials are obtained.

The dosage of the organic aliphatic dicarboxylic acid glyoxalidine salt required for the purpose of the invention is subject to variation but in general very effective results have been obtained by adding relatively minute amounts of said salt to the hydrocarbon liquid being processed. Amounts of the order of .75 part of the active salt per million parts of the hydrocarbon liquid have been effective. Excellent results have also been obtained with 2.5 p.p.m. (parts per million) of the active salt. The lower limit of the amounts used will depend upon the particular operation, and in some cases may be as low as 0.5 p.p.m. of active salt. The upper limit of the amount of active salt used will also vary, depending upon the particular operation and especially upon whether the addition of too large a quantity of the active salt may have some other disadvantage or harmful effect which would interfere with subsequent operations. A harmful effect under some conditions, depending upon whether water is present and the amounts present, as well as other factors, would be the formation of petroleum emulsions. Because of the many different types of operations where organic liquids are heated to elevated temperatures under conditions where organic deposits are formed, it is impossible to give any specific upper limit of dosage which can be adopted in every case but in most cases the preferred range is within the range of 0.5 to 8 p.p.m. of active salt and does not exceed 125 p.p.m. of the active salt. The amount of the active salt which is effective to inhibit the formation of organic deposits is referred to herein as an "anti-fouling amount."

Inasmuch as the active salts are 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 active salt or a mixture of active salts into a suitable solvent which will be compatible with the organic liquid which is to be processed.

The solvent which is used to dissolve the active effective ingredient is also subject to some variation depending upon the solubility characteristics of the particular compound employed. In some cases, even though the active compound is insoluble in a particular solvent, it will dissolve in a combination of solvents, for example, the sebacic acid derived by reacting two mols of 1(2-hydroxyethyl)-2-heptadecenyl glyoxalidine with one mol of sebacic acid at a temperature of about 133° C. for about 5 to 15 minutes is soluble in 100% denatured alcohol, soluble in Indocene 90 (a petroleum fraction high in aromatic compounds and naphthas), soluble in 99% isopropanol, insoluble in virgin gas oil and soluble in xylene. This product dissolves satisfactorily in a mixture of xylene and naphtha. In general, for most refinery operations excellent results have been obtained by dissolving the active salt in a highly aromatic hydrocarbon solvent.

A concentrate which indicates the best mode for the practice of the invention has the following composition, hereinafter referred to as composition A:

Ingredients:	Percent by weight
1-hydroxyethyl-2-heptadecenyl imidazoline sebacate	12.5
Bronoco Hi Sol	87.5

The Bronoco Hi Sol is a highly aromatic hydrocarbon solvent having the following specifications:

	ASTM Method	Specification	Typical
Gravity API at 60° F.	D287-39	10-12°	13.8°.
Specific Gravity at 60° F.		1.000-0.9340	0.9738.
Gallon Weight, lbs.		8.328-7.778	8.11.
Color	NPA	4 max.	2.0.
Corrosion	D-484-40	Neg.	Neg.
Flash Point, C.O.C.	D-56-36	200-F. Min.	226° F.
Kauri Butanol Value	D1133-50T	96 cc. Min.	99.4 cc.
Pour Point			−40° F.
Mixed Aniline Point	D1012-49T	20° C. Max.	13.3° C.
Percent Aromatics	D875-46T	95% Min.	99.2.
Distillation, ° F.	D86-46		
IBP		400 min.	403.
5%			409.
10%			420.
20%		420-440	436.
30%			450.
40%			459.
50%		460-480	470.
60%			480.
70%			491.
80%		490-510	503.
90%			520.
95%			540.
End Point		600 max.	578.

The following examples illustrate the practical application of the invention in petroleum refinery operations.

EXAMPLE I

This test was conducted in a refinery located in the southern area of the United States. In the particular part of the refinery with which the problem was concerned were two heat exchanging systems which handled crude stock from a desalting process. Prior to being fed into the exchanger systems the crude was placed into a storage tank.

Due to the presence of hydrocarbon deposits on the surfaces of the exchangers, operations were materially impeded and the heat transfer capacity of the exchangers was well below that of clean, deposit-free system. The exchanger system consisted of three pieces of equipment, the first unit comprising one exchanger, and the second being composed of two exchangers having a parallel flow connection. The first unit was connected to the second so that the crude stock flowed into the first unit and directly into the second.

The normal operating outlet temperature of the first exchanger after cleaning was between 235° F. to 245° F., but at the start of the test it was only 210° F. The secondary unit, when free of deposits, would normally

operate at 300° F. but before starting the test it was running at 292° F.

Composition A was fed into the crude stock ahead of the storage tank at 15 p.p.m. At the ends of the first week the outlet temperature of the first exchanger unit had risen to 227° F. At the end of five weeks the entire exchanger system was operating at normal temperatures which indicated a complete clean-up of the deposits which were fouling these units.

After five weeks the units were taken down for cleaning and turn-around. Inspection of the dismantled equipment revealed that the interior sides were clean except for minor deposits in dead areas. Due to the cleanliness of the system, shutdown time was only 10 days instead of the usual 14 days.

After the unit was placed back in operation the feeding of composition A was continued and was subsequently reduced to 5 p.p.m. Even at this low dosage the system remained at high operating temperatures which indicated an absence of recurrence of deposits.

EXAMPLE II

A series of tests were conducted in a large midwestern refinery on several parts of the processing units where organic deposits were evident.

(A) *Toluene extraction tower and stripper*

This process consisted of mixing phenol and toluene concentrate in an extractor. The phenol extracted impurities from the toluene; raffinate was subsequently removed. After this step the mixture was sent to a stripper where the toluene was removed from the phenol by distillation. The remaining phenol was recycled to the extractor for further use.

Deposits in the phenol circuit were causing an excessive amount of phenol to be lost. These deposits were coke-like in nature and were sloughing off from the high temperature areas of the equipment. The entire system operated over a wide range of temperatures, viz., 230° F. to 425° F.

The test was conducted over a period of several months with the average dosages of composition A being at about 25 p.p.m., fed into the phenol makeup. An additional 5 to 10 p.p.m. was intermittently fed into the phenol circuit based on the toluene production.

At the end of the first two weeks the phenol was heavily laden with deposits. After this period the phenol was clean and very little was required to go to waste because of excess deposits. The system remained clean and operated efficiently all during the remainder of the test.

(B) *Application to preheater section of fluid catalytic cracking tower*

This test was run on a preheater section of fluid catalytically cracking fractionating tower. Difficulty was encountered due to deposits building up on the heat exchanger equipment. The circulation rate of oil through the system was 30,000 barrels per day. Due to excessive hydrocarbon deposits in the heat exchangers the operating temperatures were about 260° F. with the normal operating temperature being approximately 370° F.

Treatment was begun using 10 p.p.m. of composition A which was pumped with the oil throughout the preheater section. At the end of 70 days the operating temperatures had reached 360° F. Shortly afterwards the equipment was taken down for cleaning and inspection. The equipment was practically free from deposits and the small amounts remaining were easily removed.

EXAMPLE III

In a large midwestern refinery organic deposits were being encountered in heat transfer units which were used in conjunction with a furfural extraction system. This system processed the following types of organic hydrocarbon liquids: intermediate distillates, paraffin distillates, decanted oil, vacuum cylinder stock and deasphalted cylinder stock. The exchange units after cleaning would normally operate for a month or less before the heat transfer coefficients would become so low that shutdown would be necessary.

At the start of the test composition A was added at 20 p.p.m. This treatment was continued for 25 days and the dosage dropped to 15 p.p.m. The dosage was continued at 15 p.p.m. and at the end of 75 days dropped to 5 p.p.m. The unit operated for a total of 115 days before shutdown.

The system was cleaned and put back in operation using a treatment of 10 p.p.m. of composition A. The unit ran continuously for five months without any evidence of fouling.

It will be understood that other salts of the type described can be employed in the practice of the invention. These salts can be added directly to the hydrocarbon liquid being processed. As previously indicated, however, the amounts required are so small that it is preferable to prepare a solution of the active ingredient containing about 5 to about 15% by weight thereof, the remainder being a suitable solvent which dissolves the active ingredient and is miscible with the medium to which the solution is to be added.

It will be understood that some variations can be made in the preparation of the active ingredients and in the procedures employed in using them. As examples of other long chain aliphatic dicarboxylic acids which can be reacted with any of the glyoxalidines previously described there may be mentioned the acids known in the trade as VR fatty acid and VR–1 acid. VR fatty acid is an organic carboxy acid material which is a vegetable residue resulting from the distillation of soap stock. This material contains ester bodies and has the following characteristics:

Acid value	45
Saponification value	150
Iodine value	100
Color (Bartlett)	13
Viscosity (Zahn G_5 at 75° C.) ——seconds——	15

VR–1 acid is a mixture of polybasic acids with an average molecular weight of about 1000. It has an average of slightly less than two carboxylic acid groups per molecule. It is a by-product from the production of sebacic acid by the caustic fusion of castor oil, consists principally of polymerized linoleic acid, contains dimerized, trimerized and higher polymerized linoleic acid, and is a dark amber, rather viscous liquid. A typical sample of VR–1 acid has the following analysis:

Acid number	150
Iodine number	36
Saponification number	172
Unsaponifiable matter ——percent——	3.7, 3.5
Moisture content ——do——	0.86

In the practice of the invention it is very often desirable to start the treatment with the chemicals employed for the purpose of the invention at a higher dosage, say 20 to 30 p.p.m. of a composition, such as composition A, and then gradually reduce the dosage to the point where fouling of the apparatus is just eliminated.

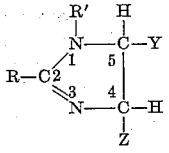
The pH of the liquid being treated can vary rather widely. Systems with a pH as low as 0.6 have been successfully treated. Other systems with a pH on the alkaline side, for example, around pH 8, have been treated satisfactorily. Higher pH conditions, such as pH 10, can be employed but are not normally encountered in most refinery operations.

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

Examples of specific types of apparatus to which the chemical compositions of the invention can be added during petroleum processing are fractionating towers, strip-

ping 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.

The term "glyoxalidine" refers to a compound having the following structural formula



wherein R is an aliphatic hydrocarbon radical; R', Y and Z are either hydrogen or an aliphatic group, it being understood that for the purpose of the present invention R, R', Y and Z are further restricted in the manner previously described. It should also be noted that in the preferred compounds of the present invention R is composed of carbon and hydrogen atoms, Y and Z are either hydrogen or groups consisting of carbon and hydrogen, and R' is either hydrogen, a group consisting of carbon and hydrogen, a group consisting of carbon, hydrogen and nitrogen, or a group consisting of carbon, hydrogen and oxygen. In other words, in the preferred compounds with respect to R' the atoms in the group are selected from the group consisting of hydrogen, carbon, nitrogen and oxygen.

The invention is hereby claimed as follows:

1. In a process of refining a hydrocarbon liquid at a temperature in excess of about 225° F., wherein high temperature carbonaceous deposits are formed from said liquid in petroleum refinery apparatus of the type including fractionating towers, stripping columns, debutanizers, depropanizers, deethanizers, heat exchangers, reboilers, and extractors, the method of operation which comprises incorporating with the hydrocarbon liquid supplied to said apparatus an anti-foulnig amount of a salt of an organic aliphatic dicarboxylic acid containing at least 10 carbon atoms in a hydrocarbon structure and a glyoxalidine wherein the carbon atom in the 2-position is linked to a higher aliphatic hydrocarbon group containing at least 8 carbon atoms, the carbon atom in the 4-position is linked to a member from the group consisting of hydrogen and lower aliphatic hydrocarbon groups containing not more than 6 carbon atoms, the carbon atom in the 5-position is linked to a member from the group consisting of hydrogen and lower aliphatic hydrocarbon groups containing not more than 6 carbon atoms, there being at least one hydrogen atom on each of the carbon atoms in the 4- and 5-positions, and the nitrogen atom in the 1-position is linked to a member from the group consisting of hydrogen and lower aliphatic groups containing not more than 6 carbon atoms, said last named lower aliphatic groups being composed of atoms from the group consisting of hydrogen, carbon, nitrogen and oxygen.

2. A process as defined in claim 1, wherein said hydrocarbon liquid is refined at a temperature within the range of about 225° F. to 800° F.

3. In a process of refining a hydrocarbon liquid at a temperature in excess of about 225° F., wherein high temperature carbonaceous deposits are formed from said liquid in petroleum refinery apparatus of the type including fractionating towers, stripping columns, debutanizers, depropanizers, deethanizers, heat exchangers, reboilers, and extractors, the method of operation which comprises incorporating with the hydrocarbon liquid supplied to said apparatus an anti-fouling amount of a sebacic acid salt of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.

4. In a fluid catalytic process of cracking oil, wherein high temperature carbonaceous deposits are formed from the oil in the preheater section of a fluid catalytic cracking fractionating tower, the method of operation which comprises incorporating with the oil feed to the preheater section an anti-fouling amount of a salt of an organic aliphatic dicarboxylic acid containing at least 10 carbon atoms in a hydrocarbon structure and a glyoxalidine wherein the carbon atom in the 2-position is linked to a higher aliphatic hydrocarbon group containing at least 8 carbon atoms, the carbon atom in the 4-position is linked to a member from the group consisting of hydrogen and lower aliphatic hydrocarbon groups containing not more than 6 carbon atoms, the carbon atom in the 5-position is linked to a member from the group consisting of hydrogen and lower aliphatic hydrocarbon groups containing not more than 6 carbon atoms, there being at least one hydrogen atom on each of the carbon atoms in the 4- and 5-positions, and the nitrogen atom in the 1-position is linked to a member from the group consisting of hydrogen and lower aliphatic groups containing not more than 6 carbon atoms, said last named lower aliphatic groups being composed of atoms from the group consisting of hydrogen, carbon, nitrogen and oxygen.

5. In a fluid catalytic process of cracking oil, wherein high temperature carbonaceous deposits are formed from the oil in the preheater section of a fluid catalytic cracking fractionatnig tower, the method of operation which comprises incorporating with the oil feed to the preheater section an anti-fouling amount of the diglyoxalidine acid salt of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine and sebacic acid.

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