United States Patent Office 3,567,623
Patented Mar. 2, 1971

3,567,623

ANTIFOULANT AGENTS FOR PETROLEUM HYDROCARBONS

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No Drawing. Filed Feb. 10, 1969, Ser. No. 805,930
Int. Cl. C10g 9/12, 9/16; C23f 14/00
U.S. Cl. 208—48 15 Claims

ABSTRACT OF THE DISCLOSURE

The present invention concerns a method for reducing or eliminating fouling deposits which are encountered in the processing or purification of crude hydrocarbons, hydrocarbon streams, petrochemicals, etc., and in particular to methods for preventing the deposition of fouling deposits wherein elevated temperatures are used. This objective is achieved by the addition of an antifouling amount of the product obtained by reacting an alkylene polyamine-aliphatic carboxylic acid reaction product with a lower aldehyde to the material being processed.

BACKGROUND OF THE INVENTION

In the processing of petroleum hydrocarbons and feedstocks such as petroleum processing intermediates, petrochemicals and petrochemical intermediates, e.g., gas, oils and reformer stocks, the hydrocarbons are commonly heated to temperatures in excess of 250° F. Similarly, such petroleum hydrocarbons are frequently employed as heating mediums on the "hot side" of heating and heat exchange systems. In both instances, the petroleum hydrocarbon liquids are subjected to elevated temperatures which produce a separate phase known as fouling deposits, within the petroleum hydrocarbon. In all cases, these deposits are undesirable by-products. In many processes, the deposits reduce the bore of conduits and vessels to impede process throughput, impair thermal transfer, and clog filter screens, valves and traps. In the case of heat exchange systems, the deposits form an insulating layer upon the available surfaces to restrict heat transfer and necessitate frequent shut-downs for cleaning. Moreover these deposits reduce throughput, which of course, results in a loss of capacity with a drastic effect in the yield of finish product. Accordingly, these deposits have caused considerable concern to the industry.

While the nature of the foregoing deposits defies precise analysis, they appear to contain either or combinations of carbonaceous phases which are coke-like in nature, polymers or condensates formed from the petroleum hydrocarbons or impurities present therein and salt formations which are primarily composed of magnesium, calcium and sodium chloride salts. The catalysis of such condensates has been attributed to metal compounds such as copper or iron which are present as impurities. For example, such metals may accelerate the hydrocarbon oxidation rate by promoting degenerative chain branching, and the resultant free radicals initiated oxidation and polymerization reactions which form gums and sediments. It further appears that the relatively inert carbonaceous deposits are entrained by the more adherent condensates or polymers to thereby contribute to the insulating or thermal opacifying effect.

Fouling deposits are equally encountered in the petrochemical field wherein the petrochemical is either being produced or purified. The deposits in this environment are primarily polymeric in nature and do drastically affect the economies of the petrochemical process. The petrochemical processes include processes ranging from those where ethylene or propylene, for example, are obtained

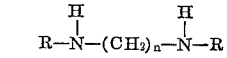
to those wherein chlorinated hydrocarbons are purified.

Accordingly, it is an object of the present invention to provide antifoulants which greatly reduce fouling deposits in liquid petroleum hydrocarbons during the exposure of such hydrocarbons to elevated temperatures and in turn reduce the formation of deposits and coatings which impede heat transfer.

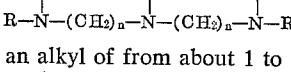
GENERAL DESCRIPTION OF THE INVENTION

The present inventor discovered that the above described objective could be attained by the use of a specially prepared reaction product. The reaction product as utilized according to the present invention is obtained by reacting at least one alkylene polyamine with a sufficient quantity of at least one aliphatic carboxylic acid to produce a salt of said amine and said acid. The consequence of the reaction between the acid and the amine is such that a salt is formed which is of such a nature that the amine reactant is decharacterized to the extent that the likelihood of an amine-aldehyde condensation polymerization is substantially eliminated. After sufficient reaction time and when the salt as above described is attained, the salt is further reacted with a lower aldehyde until all of the aldehyde added to the medium has reacted to produce as the final product. The reaction sequence may be modified slightly. For example, during the initial reaction between the amine and the acid only a portion of the amine can be reacted with the acid. The remaining portion of the amine is then added and after its addition, the aldehyde can be charged into the reactor. The antifoulants which have been found to be most effective are those which are prepared by the reaction from 0.5 to 2 equivalent weights of acid and from about 0.5 to 2 equivalent weights of aldehyde per equivalent weight of polyamine. However, the most preferred reaction products are prepared by reacting one equivalent weight of the acid with two equivalent weights of the amine and subsequently reacting the product obtained with one equivalent weight of aldehyde.

The alkylene polyamines which have been found to yield effective products are the substituted and unsubstituted alkylene polyamines, such as ethylene diamine and 1,3-diamino propane, and the substituted and unsubstituted polyalkylene polyamines such as diethylene triamine. The alkylene and polyalkylene polyamines prescribed for use by the present invention may be generally prescribed by the generic formulas which are as follows:



and



wherein R is an alkyl of from about 1 to 24, and preferably 12 to 24 carbon atoms or hydrogen and *n* represents an integer of from 1 to 4.

The fatty acids which are used according to the present invention to produce the reaction products can be generally described as "tall oil head." As is well known, tall oil heads are composed primarily of a mixture of organic saturated and unsaturated acids with the unsaturated predominating. The most commonly known tall oil head consists of a mixture of oleic acid, nonconjugated linoleic acid, conjugated linoleic acid and saturated fatty acids. As exemplary of the tall oil heads may be mentioned a number of commercially available products. One such product contains approximately 46 percent oleic acid, 36 percent nonconjugated linoleic acid, 6 percent conjugated linoleic acid, 4 percent palmitic (saturated acid), 4 percent rosin acids such as pimaric acid and

abietic acid. The remaining 4 percent by weight consists of sterols, ketones and lactones. Another commercially available tall oil head which is quite similar in constitution as that previously described consists of 51 percent by weight of oleic acid, 41 percent of conjugated linoleic acid, 6 percent of conjugated diene linoleic acid and 2 percent saturated acids. A third commercially available tall oil head which is somewhat different from the two initially described, consists of 52 percent by weight of oleic acid, 8 percent by weight of conjugated linoleic acid, 36 percent by weight of nonconjugated linoleic acid and 4 percent saturated acids. Although the tall oil heads which are used according to the invention have been described with three different examples, there are many others which are available and which consist basically of unsaturated aliphatic acids. The acids may be generally described as possessing from 8 to 22 carbon atoms. The tall oil heads which are referred to by this disclosure are well known to the worker in the art and accordingly, further description is not deemed necessary.

The aldehydes or more specifically the lower aldehydes which are utilized according to the present invention are well known and include such aldehydes as formaldehyde, acetaldehyde, etc. The preferred aldehyde for producing the reaction product is paraformaldehyde since this compound yields the most consistent reaction product.

The procedure utilized to produce the antifoulant of the present invention is as follows. Initially the amine compound is charged into a reactor which is modified so as to allow for the vacuum distillation of the reaction medium. To the reactor containing the amine is added with agitation the tall oil head. The addition is accomplished slowly and over a 5 to 15 minute period. During this time the temperature of the reaction medium is increased to from about 180 to 230° F. This temperature is maintained for a period ranging from about one-half hour to one and one-half hours. After this period has lapsed, the aldehyde is added to the reaction medium over a short period of time to insure adequate mixing and proper reaction. This addition period may range anywhere from fifteen minutes to thirty minutes. During the addition of the aldehyde an exotherm may develop; however the reaction is controlled to assure that the temperature does not exceed 250° F. This temperature is maintained for a period of 60 to 90 minutes, after which a vacuum is applied and increased to approximately 180 to 250 mm. Hg. The temperature of the reaction medium is then increased over a two hour period to a range of approximately 360 to 450° F. with the proviso that the temperature be approximately 280 to 330° F. by the end of the first hour. The vacuum is then increased slightly and these conditions are maintained for approximately 10 to 80 minutes after which the reaction medium is cooled in the vacuum as quickly as possible. When the temperature drops to about 160 to 230° F., the vacuum is broken and if desired, a solvent for the reaction product may be added.

The antifoulant of the present invention has found successful use in preventing deposits in many different type environments. The use range, that is the feed rate, depends entirely upon the particular problems of the respective processes and, of course, the type hydrocarbons or crude oils being treated. However, a feed range of approximately 0.5 to 100 parts by weight of the antifoulant per million parts by weight of the hydrocarbon being processed has been found to be effective in combating the fouling problems normally encountered.

The reaction product may be added to the hydrocarbon stream in its concentrated form, or, in order to insure proper distribution of the reaction product throughout the hydrocarbon stream, the reaction product may first be dissolved in organic solvents such as the aromatic and aliphatic petroleum solvents, and the diluted version obtained can be added to the crude or refined hydrocarbon stream. Since the reaction product is highly soluble in solvents such as the aromatic naphtha solvents and kerosene, the desired reaction product concentration in the solvent can be easily prepared.

Having thus generally described the invention, specific embodiments of the invention will be set forth below. However, these specific embodiments are intended to be representative of the invention only and not to be construed as limitative thereof.

SPECIFIC EMBODIMENTS

Example 1

The reactants used to produce the antifoulant of this example were as follows:

(1) a polyalkylene polyamine having the formula

$$CH_3(CH_2)_{17}—NH—(CH_2)_3—NH_2$$

(2) a tall oil head having the following composition:

46% oleic acid
36% nonconjugated linoleic acid
6% conjugated linoleic acid
4% palmitic acid
4% rosin acid
4% sterols, ketones, lactones, etc.

(3) paraformaldehyde

One hundred and fifty-seven pounds of the polyamine described by formula above was charged into a reactor which had been fitted with a vacuum distillation assembly. To the polyamine was added with agitation one-hundred and twenty-six pounds of the tall oil head. The addition was such as to take place over a 12 minute period. The reaction medium was then heated to a temperature of approximately 200° F. and maintained at this temperature for approximately one hour. After the one hour period had elapsed, 14.5 lbs. of paraformaldehyde was added to the reaction medium over a period of 20 minutes. An exotherm developed and was controlled so as to maintain the temperature below 210° F. A temperature of 205° F. was maintained for 75 minutes after which a vacuum was applied and increased to 200 mm. Hg. The temperature then was increased to about 390° F. over a period of two hours with the temperature being controlled so as to insure a temperature of at least 280° F. by the end of the first hour. After the two hour period, the vacuum was increased to 20 mm. Hg. These conditions were maintained for approximately 50 minutes. After the 50 minutes had elapsed, the reaction medium was cooled under vacuum and at 195° F. the vacuum was broken. At this point a high aromatic naphtha solvent was added to the reaction medium and the reaction product was dissolved therein to produce 1,113 lbs. of a 25 percent solution.

Example 2

The reactants used to produce the product of this example were as follows:

(1) an N-alkyl trimethylene diamine wherein the alkyl group contained 8 carbon atoms
(2) a tall oil head comprising the following composition:

51% oleic acid
41% conjugated linoleic acid
6% conjugated diene linoleic acid
2% saturated acids

(3) paraformaldehyde

58.1 pounds of the polyamine were charged into a reactor fitted with a vacuum distillation assembly. To the polyamine was added with agitation and over a 15 minute period 50 pounds of the tall oil head. The temperature of the reaction medium was increased to 200° F. and maintained at this temperature for approximately 1 hour. After the lapse of the one hour period, paraformaldehyde was added to the reaction medium over a 15 minute period. An exotherm developed but the temperature was

maintained below 210° F. during the addition. The temperature was then held at 205° F. for 75 minutes after which a vacuum was applied and increased to 200 mm. Hg. The temperature of the reaction medium was then increased to approximately 390° F. over a 2 hour period with the temperature reaching about 280° F. by the end of the first hour. After this 2 hour period the vacuum was increased to 20 mm. Hg., and these conditions were maintained for approximately 15 minutes. The reaction medium was then cooled as rapidly as possible and when the temperature reached 175° F., the vacuum was broken and the product allowed to cool to room temperature.

Example 3

The reactants used to produce the reaction product of the example were as follows:

(1) diethylene triamine
(2) a tall oil head as described in Example 1
(3) paraformaldehyde

A reactor bearing a vacuum distillation assembly was charged with 100 pounds of the tall oil head and to the oil was added over a few minutes period approximately 18.25 pounds of the polyamine. The temperature of the reaction mixture was then increased to approximately 210° and held at this point for approximately 1 hour. After the one hour period another portion of the polyamine (18.25 pounds) was added to the reaction mixture and the heater turned off. After a very short interval, 5.8 pounds of paraformaldehyde was added to the reaction medium over a 5 to 15 minute period. An exotherm developed, but the temperature was maintained at about 220° F. After the addition of the paraformaldehyde was completed, the temperature was maintained at 210° F. for one hour. A vacuum was then applied and increased to a 180 mm. Hg and simultaneously the temperature was increased to 390° F. over a 2 hour period. The vacuum was increased to 20 mm. Hg and the temperature was increased to approximately 440° F. with the temperature reaching about 330° F. after the first hour. These conditions were maintained for approximately one hour after which the reaction medium was cooled to 160° F. and the vacuum broken. 115 pounds of 100 percent active material was obtained and this material was dissolved in sufficient high aromatic naphtha to make a 25 percent active solution.

Example 4

A northwestern refinery had been experiencing fouling problems on both the shell and the tube sides of its crude oil preheat exchange train. The operating temperatures of the exchange train were such as to maintain a maximum temperature of 300° F. for the crude oil being processed.

Fouling deposit samples were taken from various sections of the train and analyzed to ascertain whether the problem was due to polymer or salt deposits or whether the problem was due to a combination of the two. The analyses ascertained that at certain areas of the train, the fouling deposits from one section were composed primarily of polymeric materials while the deposits from a different section of the train were found to be composed primarily of salt. In still another portion of the train, the deposits were found to be a combination of the two foulants.

Accordingly, it was recognized that any antifoulant which was to be utilized must be capable of controlling deposition of both polymeric materials and salt otherwise a combination of treatments would be necessary. After a careful study of the process system and the conditions for processing, it was recommended that a 25% active solution of the antifoulant as obtained in Example 1 be added to the crude oil entering the preheat exchange train at a feed rate of 30 parts by weight of antifoulant per million parts by weight of crude oil. After a period of two weeks, the feed rate was to be reduced to 24 p.p.m.

This feed rate was to be maintained for a period of 21 days after which the feed rate was again reduced to approximately 18 p.p.m. which was to be the normal feed.

The recommended procedure was followed and the various conditions, i.e., heat transfer and pressure consistency which indicate deposition of fouling deposits were closely observed. The pressure of the system remained constant indicating that no flow impeding fouling deposits were developing. Moreover, the heat transfer efficiency of the preheater train had not fallen off which also indicated the fouling deposition was not occurring.

Upon shutdown of the system after three months, the train was inspected for fouling deposits. Although some salt deposition was found, the system was considered to be in excellent condition as compared to what had been originally experienced.

The antifoulant of the present invention was so successful in combating foulding deposits that the feed rate was eventually decreased to 9 p.p.m. with the same excellent results being obtained.

Example 5

A refinery which processed 21 to 24,000 barrels per day of Canadian light crude oil was charging the system through a desulfurizor unit. The charge system contained six charge/effluent exchangers and one large multiburner, single pass and the reactor.

Careful observance of the process revealed that due to contaminated crude, heat transfer was dropping off in the exchangers which in turn required increased firing load in the furnace. The fouling was so severe within two weeks that it was necessary to cut back the crude feed to 17,500 barrels per day because of furnace capacity.

At this point a 25% solution of the antifoulant of Example 1 was fed at a rate of approximately 30 p.p.m. with the feed points just downstream of the charge pump.

After just two days of feeding the antifoulant, heat transfer had recovered to a point where the crude charge could be increased back to normal.

In addition to the above examples of successful use of the present invention, the invention has been used with great success in other sections of refinery streams such as in the light ends column refluxor systems, the Cat/Poly Depropanizor Towers. Moreover, the invention has found use in the petrochemical field.

Having thus described the invention, what is claimed is:

1. A method for reducing the quantity of fouling deposits formed during the processing at elevated temperatures of a petroleum hydrocarbon or a petrochemical which comprises adding thereto an antifouling amount of the reaction product obtained by:

(1) reacting at least one alkylene polyamine with a sufficient quantity of at least one aliphatic carboxylic acid to produce a salt of said amine and said acid, said salt being of such nature that the amine reactant is decharacterized to the extent that the likelihood of an amine-aldehyde condensation polymerization is substantially eliminated, and

(2) reacting the salt with a lower aldehyde.

2. A method according to claim 1 wherein only a portion of amine to be reacted is reacted initially with said acid and wherein the remaining portion is added to the initial reaction product and allowed to react at a time prior to the addition of the aldehyde.

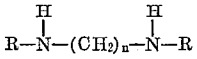
3. A method according to claim 1 wherein the alkylene polyamine is a polyalkylene polyamine and said acid is a mixture of acids composed primarily of unsaturated acids having from 8–22 carbon atoms.

4. A method according to claim 1 wherein from about 0.5 to 2 equivalent weights of acid and from about 0.5 to 2 equivalent weights of aldehyde per equivalent weight of polyamine are reacted.

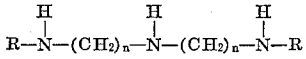
5. A method according to claim 1 wherein the reactants are reacted in the ratio of 1 equivalent weight of

acid, 2 equivalent weights of amine and 1 equivalent weight of aldehyde.

6. A method according to claim **1** wherein the polyamine possesses a formula selected from the group consisting of:



and



wherein R is an alkyl of from 12 to 24 carbon atoms or hydrogen, and *n* represents an integer of from 1 to 4.

7. A method according to claim **8** wherein the acid is a refined tall oil head.

8. A method according to claim **7** wherein the tall oil head is composed primarily of a mixture of oleic acid, nonconjugated linoleic acid and conjugated linoleic acid.

9. A method according to claim **7** wherein the lower aldehyde is paraformaldehyde.

10. A method according to claim **9** wherein from about 0.5 to 2 equivalent weight of tall oil head and from about 0.5 to 2 equivalent weight of paraformaldehyde per equivalent weight of polyamine are reacted.

11. A method according to claim **10** wherein said reaction product is added to said hydrocarbon in an amount of between 0.5 to 100 parts by weight per million parts by weight of said hydrocarbon.

12. A method according to claim **11** wherein 1 equivalent weight of tall oil head and 1 equivalent weight of paraformaldehyde per equivalent weight of polyamine are reacted.

13. A method for reducing fouling deposits experienced during the processing at elevated temperatures of a petroleum hydrocarbon or a petrochemical which comprises adding thereto an effective antifouling amount of the reaction product obtained by reacting approximately two equivalent weights of a polyamine having the formula

$$CH_3(CH_2)_{17}—NH—(CH_2)_3—NH_2$$

with approximately one equivalent weight of a refined tall oil head to form a salt of said polyamine, and reacting the salt obtained with about 1 equivalent weight of a paraformaldehyde to obtain the reaction product.

14. A method according to claim **13** wherein from about 0.5 to about 100 parts by weight of the reaction product per million parts by weight of the hydrocarbon is added to said hydrocarbon.

15. A method according to claim **14** wherein the reaction product is in a solvent solution.

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U.S. Cl. X.R.

44—73; 252—401, 405