

1

2,873,253

METHOD OF INHIBITING THE DEPOSITION OF FORMALLY SOLID PARAFFINS FROM A PETROLIFEROUS FLUID CONTAINING SAME

Roy D. Stanphill, Pasadena, Tex., assignor, by mesne assignments, to Esso Research and Engineering Company, Elizabeth, N. J., a corporation of Delaware

No Drawing. Application October 22, 1957
Serial No. 691,558

10 Claims. (Cl. 252—8.55)

This invention relates to suspending agents for use in the suspending of normally solid paraffinic hydrocarbons in petroliferous fluids. More particularly, the present invention relates to suspending agents for preventing the deposition of normally solid hydrocarbons contained in petroliferous fluids and to a process for inhibiting the deposition of such normally solid paraffins from petroliferous fluids during the production, transportation, storage, etc., of the same.

This application is a continuation-in-part of Stanphill application Ser. No. 538,811, filed October 5, 1955, now abandoned, and entitled "Suspending Agents."

Petroliferous fluids, produced from oil and gas wells will frequently contain normally solid paraffinic hydrocarbons which tend to accumulate in the well bore and in the equipment utilized in producing the petroliferous fluid. In addition, the normally solid paraffins frequently tend to accumulate in transportation lines, storage vessels and other equipment wherein the petroliferous fluids are processed. This presents a serious problem in that the deposition of paraffins interferes with the production, transportation, storage, processing, etc. of the petroliferous fluids containing such paraffinic materials. Paraffin deposition may proceed to the point where production is completely interrupted.

In the past it has been proposed to overcome this problem through the use of mechanical devices for removing deposited paraffins, through the use of solvents for the paraffins, etc. However, the results that have been obtained have not been entirely satisfactory.

An object of the present invention is the provision of suspending agents for normally solid paraffinic hydrocarbons contained in petroliferous fluids.

Another object is the provision of a process for inhibiting the deposition of normally solid paraffinic hydrocarbons from petroliferous fluids during the production, transportation, storage and processing of such fluids.

A further object is the provision of a process for removing deposits of normally solid paraffinic hydrocarbons.

These and other objects are attained, in general, through the provision of a fatty acid derivative prepared by reacting a water-insoluble fatty acid with a primary or secondary amine, the organic radicals attached to the nitrogen of the amine containing not more than about two carbon atoms per organic radical, said amine being reacted with said fatty acid at a temperature of not more than about 200° F. in an amount sufficient to provide an amine salt having the hereinafter described solubility characteristics. The fatty acid derivative may be added to a petroliferous fluid containing normally solid paraffins in an amount sufficient to prevent deposition of a substantial portion of such paraffins or may be brought into

2

contact with a deposit of normally solid paraffins in the presence of a hydrocarbon in an amount sufficient to suspend the deposited paraffins in the hydrocarbon.

The fatty acids to be used in preparing the derivatives of the present invention are mono- and polycarboxylic acids which are substantially completely insoluble in water. Representative carboxylic fatty acids which may be used include monocarboxylic fatty acids containing from about 12 to 18 carbon atoms such as lauric acid, tridecoic acid, myristic acid, palmitic acid, marjaric acid, stearic acid, oleic acid, linoleic acid, linolenic acid, etc. and mixtures thereof, polycarboxylic acids such as brassylic acid, thapsic acid, etc. and mixtures thereof. The fatty acids may be used in purified form if desired or, preferably, naturally occurring oils containing the same may be used such as, for example, coconut oil, palm oil, tall oil, oiticica oil, etc. and mixtures thereof. Preferred starting materials for the present invention include tall oil and also the residue obtained from the production of sebacic acid by the heat degradation of castor oil, such residue primarily containing water insoluble dimeric fatty acids. A description of this product will be found, for example, in the Cheetham et al. Patent No. 2,267,269. The residue is an amber colored viscous residue containing long chained carboxylic acids (primarily dimeric fatty acids), such residue having an acid number between about 40 and 200, having an iodine number between 30 and 60, having an average molecular weight of about 1,000, and being the non-volatile material remaining from the vacuum distillation at 270° C. under 4 millimeters pressure of the by-product acids obtained during the preparation of sebacic acid from castor oil.

The amines to be used in accordance with the present invention for reaction with the water insoluble carboxylic acid are primary and secondary amines having attached, to the nitrogen of the amine, organic radicals containing not more than about 2 carbon atoms per organic radical. Representative of the amines of this nature which may be used are monomethyl amine, dimethyl amine, dimethanol amine, monoethyl amine, diethyl amine, monoethanolamine, diethanol amine, ethylene diamine, dimethyltri-amine, diethylenetriamine, triethylenetetraamine, tetraethylenepentamine, etc. and mixtures thereof. A preferred amine which is used with the most satisfactory results in monoethanolamine.

The reaction between the amine and carboxylic acid should be conducted at a temperature of not more than about 200° F. and is preferably initiated at room temperature. Heat is normally evolved during the reaction, the rise in temperature normally being such that the temperature at the end of the reaction is about 50° F. higher than the initial reaction temperature. Accordingly, when the reaction is initiated at temperatures above room temperature care should be taken to avoid a rise in temperature during reaction to a temperature in excess of about 200° F. This is necessary in that the desired reaction products of the present invention are amine salts which are dehydrated to form amides at temperatures above about 200° F.

The carboxylic acids are highly viscous or solid materials at room temperatures and, accordingly, the reaction is preferably (although not necessarily) conducted in solvent solution. Any suitable organic solvent may be used for this purpose including, for example, organic aromatic hydrocarbons such as benzene, toluene, xylenes, and mixtures thereof; chlorinated hydrocarbons such as carbon tetrachloride, trichloroethane, dichloropentane,

3

dichlorodiethylether, etc. and mixtures thereof. When a solvent is to be used, it is preferable to first dissolve the fatty acid in the solvent and to then add the amine to the thus prepared solution with agitation. It is preferable to use about a 5 to 40 percent solution of the fatty acid or fatty acid-containing material. The reaction proceeds rapidly and is normally substantially complete on addition of the amine.

Generally speaking, it may be stated that from about 10 to 40 parts of amine should be reacted with about 90 to 60 parts of fatty acid, the amine and fatty acid being reacted in amounts sufficient to provide a reaction product having the hereinafter defined solubility characteristics. For example, when the dimeric fatty acid-containing residue is to be used, about 10 to 25 parts by weight of amine should be reacted with about 90 to 75 parts by weight of residue and, preferably, about 15 to 20 parts of amine are reacted with about 85 to 80 parts of the residue.

As indicated, the amount of amine to be employed will vary with the nature of the fatty acid employed since the fatty acid derivatives of the present invention will have both hydrophobic and hydrophilic properties. In co-pending application Ser. No. 538,811, the solubility characteristics of the derivatives of the present invention are defined in terms of the water-solubility of the product obtained by reacting from about 20 to 35 volume percent of monoethanolamine (preferably 25 to 30 volume percent) with, correspondingly, about 80 to 65 volume percent (preferably 75 to 70 volume percent) of the tall oil. Such reaction products may be further defined as products having the following solubility characteristics:

(a) Water solubility—a 5% solution of the product in pure isopropyl alcohol or mixtures of isopropyl alcohol with up to 45 volume percent of water is clear whereas with greater amounts of water the solution is cloudy.

(b) Oil solubility—a 5% solution of the product in toluene or in mixtures of toluene with up to 45 volume percent of iso-octane is clear whereas with greater amounts of iso-octane a cloudy solution is formed.

That is to say, the reaction products of the present invention form a colorless 5% volume solution in a mixture of at least 55 volume percent of isopropyl alcohol with, correspondingly, not more than 45 volume percent of water and in a mixture of at least 55 volume percent of toluene with, correspondingly, not more than 45 volume percent of iso-octane.

A thus-prepared fatty acid derivative of the present invention or a mixture of two or more such derivatives is added to a petroliferous fluid containing normally solid paraffinic hydrocarbons in an amount sufficient to prevent deposition of a substantial portion of the paraffinic materials. The derivative is preferably added in the form of about a 5 to 40 percent organic solvent solution. However, if desired the fatty acid derivatives may be added directly to the petroliferous fluid without dilution.

Generally speaking, the amount of derivative to be used will be within the range of about 0.001 to about 10 volume percent of the petroliferous fluid to be treated. In general, satisfactory results are obtained through the use of about 0.001 to about 1 volume percent.

The following examples are given by way of illustration and are not intended as limitations on the scope of this invention.

EXAMPLE I

A plurality of fatty acid derivatives were prepared from monoethanolamine. A first group of fatty acid derivatives was prepared by reacting the monoethanolamine with a plurality of samples of tall oil and another group of fatty acid derivatives was prepared by reacting the monoethanolamine in various proportions with a plurality of samples of the dimeric fatty acid-containing residue described above. The proportions of monoethanol-

4

amine to tall oil, and residue comprising dimeric fatty acids are given in Table I. In preparing each of the derivatives, the fatty acid component was dissolved in an amount of xylene sufficient to provide about a 20% solution of the starting material. Next, the desired amount of monoethanolamine was added to the solution with agitation over a period of about 30 minutes. In each instance the reaction was initiated at room temperature and atmospheric pressure. In each instance, a rapid rise in reaction temperature occurred as the monoethanolamine was added, the final reaction temperature being about 140° F. The reactions were substantially complete upon addition of the monoethanolamine. However, the reaction mixtures were held at a temperature of about 140° F. for about 30 minutes after addition of the last of monoethanolamine in order to insure completeness of the reaction.

Table I-A

COMPOSITION OF CARBOXYLIC ACID DERIVATIVES

Derivative	Carboxylic Acid Component	Parts by Weight	Amine	Parts by Weight
I	Residue comprising dimeric fatty acids.	85	Monoethanolamine.	15
II	do.	80	do.	20
III	do.	70	do.	30
IV	Tall Oil	80	do.	20
V	do.	70	do.	30
VI	do.	60	do.	40
VII	do.	40	do.	60

Table I-B

SOLUBILITY OF CARBOXYLIC ACID DERIVATIVES

Derivative	Water Solubility (Clear 5 Vol. Percent Solution in a Mixture of 55 Vol. Percent Isopropyl Alcohol with 45 Vol. Percent of Water)	Oil Solubility (Clear 5 Vol. Percent Solution in a Mixture of 55 Vol. Percent Toluene with 45 Vol. Percent of Iso-octane)
I	Soluble	Soluble.
II	do.	Soluble (Slightly Hazy).
III	do.	Insoluble.
IV	do.	Soluble.
V	do.	Do.
VI	do.	Do.
VII	do.	Insoluble.

EXAMPLE II

The xylene solutions of the fatty acid derivatives prepared in Example I were tested to determine their effectiveness as paraffin suspending agents. The test employed was as follows.

A sample of a highly paraffinic crude oil from the Luling Field was centrifuged, and it was found that about 50 volume percent of the material in the crude oil sample could be separated by centrifugation. It was found that the separable solids material consisted of about 95 volume percent of paraffinic hydrocarbons and about 5 volume percent of other separable materials (primarily a water-oil emulsion). In conducting the tests, a given volume of a xylene solution of one of the derivatives of Example I was added to a portion of the crude oil sample and the resultant mixture was agitated. Thereafter, the resultant solution was centrifuged in order to separate solid materials which were not suspended by the fatty acid derivative. The results are set forth in Table II. It is to be noted from Table II that the results obtained are expressed both in terms of the percentage of separable solid materials suspended and also in terms of the percentage of paraffin suspended. This has been done in order to emphasize that it is the paraffinic hydrocarbons which are suspended in accordance with the present invention and not other types of separable solids such as oil and water emulsions.

5
Table II

Run No.	Derivative	Vol. Per- cent of Derivative Added ¹	Percent Separable Solids Suspended	Percent Paraffin Suspended
1	I	10	84	93
2	I	12.5	92	96
3	I	15	94	98
4	II	10	38	40
5	II	12.5	94	98
6	II	15	96	100
7	III	10	0	0
8	III	12.5	16	17
9	III	15	26	27
10	IV	10	0	0
11	IV	12.5	27	28
12	IV	15	59	61
13	V	10	84	93
14	V	12.5	92	96
15	V	15	94	98
16	VI	10	12	12
17	VI	12.5	45	47
18	VI	15	74	77
19	VII	10	0	0
20	VII	12.5	11	11
21	VII	15	11	11

¹ Derivative added as a 20% xylenes solution.

From Table II it will be noted that the results which were obtained were not uniform. Derivatives I to III prepared by reacting monoethanolamine with the residue comprising dimeric fatty acids were tested in runs 1 to 9. Runs 1 to 3 show that derivative I was an effective suspending agent which gives excellent results and that derivative II was an effective suspending agent at the higher concentrations (runs 5 and 6) but not at the lowest concentration (run 4). Runs 7 to 9 show that derivative III was not particularly effective as a suspending agent.

Runs 10 to 21 show the results obtained with respect to derivatives IV to VII obtained by reacting monoethanolamine with tall oil. Runs 10 to 12 show that derivative IV was only partially effective as a suspending agent at the highest concentration (run 12). From runs 13 to 15 it is seen that derivative V was an effective paraffin suspending agent giving excellent results. Runs 16 to 18 show that derivative VI gave satisfactory results at the highest concentration (run 18). Derivative VII was not an effective paraffin suspending agent as shown by the results obtained in runs 19 to 21.

Equivalent results are obtained when a reaction product of about 85 parts of the dimeric fatty acid-containing residue are reacted with about 15 parts of ethylene diamine or with about 15 parts of diethylene triamine in solvent solution at room temperature to give derivatives which are tested in the above described manner.

EXAMPLE III

As another example, about 8.5 liters of high paraffin content crude were circulated through a ½" internal diameter galvanized pipe cooled at a temperature of about 80° F. for about 96 hours. At the end of this time the pipe was weighed to determine the amount of paraffin deposited therein and was then cleaned. It was found that about 35.5 milligrams of paraffin per inch of pipe per hour had been deposited during the run. Thereafter, about 1 volume percent of derivative V (Table I) was added to the crude oil as a 20 percent solution and the test procedure was repeated. It was found that in this instance the rate of deposition was only about 9.5 milligrams per inch of pipe per hour.

The same results were obtained through the use of about 1 volume percent of derivative I.

EXAMPLE IV

A 500 barrel tank of oil was found to have a bottom deposit of about 9 inches of paraffin. About 1 gallon (i. e., about 0.005 volume percent) of a 20% xylenes solution of derivative I (Table I) was added to the stor-

6

age tank and thereafter the bottom of the storage tank was rolled (i. e., vigorously agitated) in order to agitate the deposited paraffins. The rolling lasted for about one-half hour. At the end of 1 day it was found that the deposited material amounted to less than 3 inches and was of a substantially non-paraffinic nature (i. e., consisted of emulsion, scale, impurities, etc.).

In another instance, one gallon of a 20% xylenes solution of derivative I (Example I) was added to a 500 barrel storage tank having about a 20 inch deposit of paraffin on the bottom thereof. The tank was rolled for about one-half hour. At the end of about 1 day only about 9 inches of material had again settled to the bottom of the tank, such material again being of a substantially non-paraffinic nature.

EXAMPLE V

It was found that the flow treater on an oil well in the Neches Field was foaming out of the vent line because the incoming petroliferous fluid could not follow its normal course. The contents of the barrel were heated and circulated with the addition of about 20 gallons of a 20% xylenes solution of derivative I (Table I). The gun barrel system resumed normal operation after this treatment.

What is claimed is:

1. A method for inhibiting the deposition of normally solid paraffins from a petroliferous fluid containing the same which comprises incorporating a fatty acid derivative into said petroliferous fluid in an amount sufficient to inhibit deposition of a substantial portion of said normally solid paraffins, said derivative having been prepared by reacting a water insoluble fatty acid with an amine selected from the group consisting of primary and secondary amines having attached, to the nitrogen of the amine, organic radicals containing not more than about 2 carbon atoms per radical, at a temperature of not more than about 200° F., said amine being reacted with said fatty acid in an amount sufficient to provide a reaction product forming a colorless 5 volume percent solution in (a) mixtures of at least 55 volume percent of isopropyl alcohol with water and (b) mixtures of at least 55 volume percent of toluene with iso-octane.

2. A process as in claim 1 wherein the said fatty acid derivative is added to said petroliferous fluid in solution in an organic solvent.

3. A process as in claim 2 wherein the solvent is an aromatic hydrocarbon.

4. A process as in claim 3 wherein the solvent is a chlorinated hydrocarbon.

5. A method for inhibiting the deposition of normally solid paraffins from a petroliferous fluid containing the same which comprises incorporating a fatty acid derivative into said petroliferous fluid in an amount sufficient to inhibit deposition of a substantial portion of said normally solid paraffins, said derivative having been prepared by reacting a water insoluble fatty acid with monoethanolamine at a temperature of not more than about 200° F., said fatty acid being reacted with said monoethanolamine in an amount sufficient to provide a reaction product forming a colorless 5 volume percent solution in (a) mixtures of at least 55 volume percent isopropyl alcohol with water and (b) mixtures of at least 55 volume percent of toluene with iso-octane.

6. A method for inhibiting the deposition of normally solid paraffins from a petroliferous fluid containing the same which comprises incorporating a fatty acid derivative into said petroliferous fluid in an amount sufficient to inhibit deposition of a substantial portion of said normally solid paraffins, said fatty acid derivative having been prepared by reacting about 25 to about 30 parts by weight of monoethanolamine with about 75 to 70 parts by weight of tall oil in solution in a non-reactive organic solvent at a temperature of not more than about 200° F.

7. A method for inhibiting the deposition of normally solid paraffins from a petroliferous fluid containing the same which comprises incorporating a fatty acid derivative into said petroliferous fluid in an amount sufficient to inhibit deposition of a substantial portion of said normally solid paraffins, said derivative having been prepared by reacting about 15 to 20 parts by weight of monoethanolamine with about 85 to 80 parts by weight of the dimeric fatty acid-containing residue resulting from the distillation of the by-product acids obtained in the preparation of sebacic acid from castor oil, at a temperature of not more than about 200° F.

8. A method for removing a deposit of normally solid paraffins which comprises contacting said deposit with a liquid comprising an organic hydrocarbon and a fatty acid derivative, said fatty acid derivative being present in an amount sufficient to suspend the deposited paraffins in said liquid, said fatty acid derivative having been prepared by reacting a water insoluble fatty acid with an amine selected from the group consisting of primary and secondary amines having attached, to the nitrogen of the amine, organic radicals containing not more than about 2 carbon atoms per radical, at a temperature of not more than about 200° F., said amine being reacted with said fatty acid in an amount sufficient to provide a reaction product forming a colorless volume percent solution in (a) mixtures of at least 55 volume percent of isopropyl alcohol with water and (b) mixtures of at least 55 volume percent of toluene with iso-octane.

9. A method for treating a conduit for the transmission of a paraffinic petroliferous fluid in order to remove normally solid paraffins deposited in said conduit which comprises contacting said deposited paraffins with an amount of a liquid comprising an organic hydrocarbon

and fatty acid derivative sufficient to suspend said deposited paraffins in said liquid, said derivative having been prepared by reacting a water insoluble fatty acid with an amine selected from the group consisting of primary and secondary amines having attached, to the nitrogen of the amine, organic radicals containing not more than about 2 carbon atoms per organic radical, at a temperature of not more than about 200° F., said amine being reacted with said acid in an amount sufficient to provide a reaction product forming a colorless 5 volume percent solution in (a) mixtures of at least 55 volume percent isopropyl alcohol with water and (b) mixtures of at least 55 volume percent of toluene with iso-octane.

10. A method for treating a container for paraffinic petroleum hydrocarbons in order to remove normally solid paraffins deposited therein which comprises adding to said petroleum hydrocarbon an amount of a fatty acid derivative sufficient to suspend said deposited paraffins in said hydrocarbon, said derivative having been prepared by reacting a water insoluble fatty acid with an amine selected from the group consisting of primary and secondary amines having attached, to the nitrogen of the amine, organic radicals containing not more than about 2 carbon atoms per organic radical, at a temperature of not more than about 200° F., said amine being reacted with said fatty acid in an amount sufficient to provide a reaction product forming a colorless 5 volume percent solution in (a) mixtures of at least 55 volume percent of isopropyl alcohol with water and (b) mixtures of at least 55 volume percent of toluene with iso-octane.

References Cited in the file of this patent

UNITED STATES PATENTS

2,470,831 Monson ----- May 24, 1949