United States Patent

Stanley

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[54] METHOD FOR INHIBITING FOULING IN A REFINERY PROCESS

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[52] **U.S. Cl.**.....**208/48 AA**, 203/7, 252/51.5

[51] **Int. Cl.**.....**C10g 9/16**, C10g 9/36, C23f 14/00

[58] **Field of Search**.....208/48

[56] **References Cited**

UNITED STATES PATENTS

2,666,044	1/1954	Catlin	260/80.5
2,737,752	3/1956	Catlin et al.	44/62
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3,546,097	12/1970	Tupper	208/48 AA
3,554,897	1/1971	Stanley	208/48 AA

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[57] **ABSTRACT**

Method of treating petroleum hydrocarbon liquids to inhibit the fouling of refinery process equipment involving the addition of an anti-fouling amount of an oil-soluble addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage, at least one of which component is amine free and contains from 4 to about 18 carbon atoms, one of the components contains a basic aminonitrogen in the side chain and one of the components contains a hydrocarbon-substituted-amide in the side chain.

8 Claims, No Drawings

METHOD FOR INHIBITING FOULING IN A REFINERY PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The processing of petroleum hydrocarbon liquids to effect conversion or separation is generally conducted at an elevated temperature with the petroleum feed stream coming into intimate contact with the metal surfaces of the process equipment. The feed streams frequently contain components which have a tendency to decompose or undergo a chemical reaction when in contact with the hot metal surfaces of the process equipment resulting in the formation of insoluble bodies. These insoluble bodies deposit on and adhere to the surfaces of the equipment with the result that both the heat transfer efficiency and the design throughput of the equipment are very substantially reduced.

The foregoing phenomenon has been observed with many liquid hydrocarbon streams in a wide variety of processes. The processes in question are characterized by high operating temperatures ranging from about 200°F. to 1200°F. or higher and include distillation, reforming, cracking, isomerization, hydrogenation, dehydrogenation, alkylation and polymerization of hydrocarbon fractions including naphtha, kerosene, gas oils, middle distillates, crude oils and the like. The deposit forming tendency of the oil being treated is evident not only in the principal reactor but also in associated equipment such as boilers, heat exchangers, stripping columns and the like. It will be appreciated that the economics of a process having a deposit laydown or coking problem is adversely affected not only by the loss of throughput and conversion efficiency but also by the downtime and cleanup costs incurred when the deposits are removed from the equipment.

2. Description of the Prior Art

A U.S. Pat. application, Ser. No. 681,917, filed on Nov. 9, 1967 (now U.S. Pat. No. 3,554,897) discloses a method for inhibiting fouling in a refinery process wherein the anti-foulant employed is an oil soluble basic amino-nitrogen-containing addition type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage, at least one of which component is amine free and contains from 4 to about 18 carbon atoms in an aliphatic hydrocarbon chain which in the polymer is not part of the main chain, and one of the components as it exists in the polymer containing a basic amino-nitrogen in the side chain, said copolymer containing 0.1 to 3.5 percent by weight of basic amino-nitrogen.

A U.S. Pat. application, Ser. No. 787,564, filed on Dec. 27, 1968 (now U.S. Pat. No. 3,546,097) discloses a process for inhibiting fouling in chemical processing and oil refining equipment comprising incorporating into the operation an anti-fouling amount of an admixture comprising: (a) an alkyl methacrylate copolymer containing at least one basic aminonitrogen addition type polymer and (b) at least one nitrogen containing additive selected from the group consisting of N,N'-disalicylidene-1,2-alkanediamine and p-aminodiphenyl-amine dialkanoates wherein the dialkane moiety contains from 4 to 20 carbon atoms.

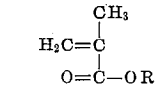
The disclosures of the foregoing applications Ser. No. 681,917 and No. 787,564 are incorporated in this application.

SUMMARY OF THE INVENTION

In its broadest aspects, the anti-fouling process of the invention involves the treatment of a petroleum hydrocarbon liquid which is intended to be exposed to an elevated temperature with an anti-fouling amount of an oil-soluble addition-type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage at least one of which components is amine free and contains from 4 to about 18 carbon atoms in an aliphatic hydrocarbon chain which in the polymer is not part

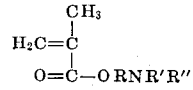
of the main chain, one of the components as it exists in the polymer containing a basic amino-nitrogen in the side chain and one of the components as it exists in the polymer containing a hydrocarbon substituted amide in the side chain, said copolymer containing from about 0.1 to 3.5 percent of said basic amino-nitrogen and from about 0.05 to 4 percent of said component containing said amide. In another aspect of the process, an anti-fouling amount of an aldehyde-amine condensation product is employed in combination with the above-described addition type copolymer. Alternatively, or in a three-component combination with the foregoing anti-foulant components a minor amount of an anti-fouling aromatic amide is employed in the process.

The oil-soluble addition-type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage is formed from derivatives of acrylic acid or an alkyl substituted acrylic acid, such as alkyl-substituted methacrylic acid. The predominant component in the copolymer is preferably a substituted ester of methacrylic acid represented by the formula:



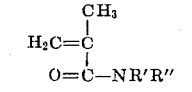
in which R is an aliphatic hydrocarbon radical having from about 4 to 18 carbon atoms. Esters of methacrylic acid within the above definition and which are suitable for preparing the anti-foulant copolymer include: butyl methacrylate, lauryl methacrylate, dodecyl methacrylate, stearyl methacrylate, octyl methacrylate and the like. A mixture of this type of methacrylate ester may be employed as the principal component of the copolymer.

The basic amino nitrogen monomeric component is represented by the formula:



in which R is an alkylene radical having from 2 to 4 carbon atoms and R′ and R″ are hydrogen or an aliphatic hydrocarbon radical having from 1 to 8 carbon atoms. Examples of preferred monomers in this class include: dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, methylethylaminoethyl methacrylate, butylaminoethyl methacrylate, hexylaminopropyl methacrylate and N,N-dimethylaminopropyl methacrylate.

The hydrocarbon-substituted amide monomeric ethylenically unsaturated component which can be employed to prepare the anti-foulant copolymer is represented by the formula:



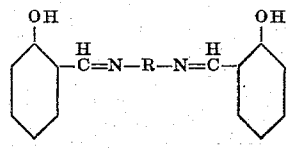
in which R′ and R″ are hydrogen, an aliphatic hydrocarbon radical having from 1 to 18 carbon atoms or a $(CH_3)_2N–R'''$- radical in which R‴ has from 2 to 4 carbon atoms. Typical monomers within this definition and which are suitable in the preparation of the anti-fouling copolymer include: N-t-octyl methacrylamide, N-butyl methacrylamide, N-di-t-octyl methacrylamide and N,N-dimethylaminopropyl methacrylamide.

The ethylenically unsaturated monomers described above are admixed in suitable proportions and polymerized by conventional bulk, solution or dispersant polymerization methods using known catalyst, such as benzoyl peroxide, and azo com-

ponents such as alpha-alpha-azo diisobutyronitrile. Convenient solvents for the polymerization reaction are high boiling hydrocarbons particularly those similar to the hydrocarbons in which the copolymers are to be used such as kerosene, naphtha and middle distillates. These polymerization processes are generally carried out in an inert atmosphere for example nitrogen or carbon dioxide at temperatures ranging from about 30°C. to 150°C. depending on the catalyst used. It is essential to carry the copolymerization substantially to completion so that no unpolymerized monomers remain in the copolymer and the proportions of each component in the final product are essentially those of the original monomer mixture. The preparation of copolymers of this type is described in U.S. Pat. No. 2,666,044 and No. 2,737,452 and the disclosures in these references are incorporated herein. The proportions and types of the foregoing monomeric components are chosen so that the copolymer produced will contain from about 0.1 to 3.5 percent of said basic amino-nitrogen and from about 0.05 to 4 percent of said component containing said amide.

An optional component in the anti-fouling process of the invention is a nitrogen-containing aromatic Schiff's base formed from the condensation of an aromatic aldehyde with an aliphatic polyamine. Aldehydes suitable for preparing the Schiff's base include benzaldehyde, 2-methyl benzaldehyde, 3-benzaldehyde, 2-methoxybenzaldehyde, 4-methoxygenzaldehyde, 2-hydroxy 6-methyl benzaldehyde, 2-hydroxy 3-methoxygenzaldehyde. Polyamines which can be employed in preparing the Schiff's base include ethylenediamine, 1;2-propylene diamine, 1,3-propylenediamine, 1,6-hexamethylene diamine, diethylene triamine, triethylenetetramine.

The preferred Schiff's base compound for use in conjunction with the copolymer of the invention is represented by the formula:



in which R is a divalent hydrocarbyl radical having from 2 to 4 carbon atoms. Representative Schiff's bases include: N,N'-disalicylidene-1,2-diaminoethane, N,N'-disalicylidene-1,2-diaminopropane and N,N'-disalicylidene-1,2-diaminobutane.

The anti-fouling process of this invention based on the addition of the above-defined addition type copolymer to the petroleum hydrocarbon liquid being treated may also employ an aromatic amide in combination with the copolymer and/or the nitrogen-containing aromatic Schiff's base. The aromatic amides are formed by the reaction of a suitable amine and organic acid or acid derivative. For example, an aromatic amine, such as diphenylamine, can be reacted with an aliphatic acid, anhydride or acid halide. Alternatively, an organic acid or acid derivative can be reacted with an aliphatic amine or diamine.

Suitable aromatic aldehydes for this reaction include: benzaldehyde, 2-methylbenzaldehyde, 3-methylbenzaldehyde, 4-methylbenzaldehyde, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, α-naphthaldehyde, β-naphthaldehyde, 2-hydroxybenzaldehyde (salicylaldehyde), 2-hydroxy-6-methylbenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde and the like.

Suitable aliphatic polyamines include: ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, 1,6-hexamethylenediamine, 1,10-decamethylenediamine, diamine, diethylenetriamine, triethylenetetramine, pentaerythritoltetramine and the like.

Suitable aromatic amines for forming aromatic amides include: aniline, phenylene-diamine, triamino-benzene, diphenylamine, o-toluidine, m-toluidine, p-toluidine, benzylamine, 2,3-toluylene-diamine, 2,4-toluylene-diamine, 2,5-toluylene-diamine, 2,6-toluylene diamine, 3,4-toluylenediamine, 3,5-toluylene-diamine, o-amino-diphenyl-amine, p-amino-diphenylamine, etc.

In general, any of the aliphatic acids, anhydrides or acid halides, straight chain or branched chain, can be reacted with the aromatic amines to produce the desired amide additives of this invention. These include particularly those acid halides and anhydrides having a carbon chain length varying between 4 and 20 carbon atoms. Useful aliphatic acid halides include the acid chlorides corresponding to the fatty aliphatic acids such as acetic, propanoic, butanoic, hexanoic, octanoic, nonanoic, decanoic, undecanoic as well as their bromine analogues. While the acid chlorides are preferred because of their activity, low cost and availability, where desired the more sluggishly reactive acids or anhydrides may be employed. The reaction conditions used in the preparation of the aromatic amides are well known and can be found in the technical or patent literature.

SPECIFIC EMBODIMENTS OF THE INVENTION

The following example illustrates the preparation of specific copolymer for the process of this invention. Unless otherwise noted, all percentages and parts are by weight.

EXAMPLE 1.

To a reaction kettle equipped with a means of providing stirring, heating, cooling and inert atmosphere is added 37.0 parts by weight of refined paraffin distillate (150 SU viscosity at 100°F.), 23.7 parts by weight of butyl methacrylate, 4.7 parts by weight of dimethylaminoethyl methacrylate, 58.5 parts by weight of lauryl methacrylate, 29.2 parts by weight stearyl methacrylate, 0.9 parts by weight of N-t-octylacrylamide, and 0.14 parts by weight lauryl mercaptan. The mixture is stirred and heated to 170°F. over a period of 0.7 hours while purging with nitrogen gas. At this time 0.16 parts by weight of azobisisobutyronitrile slurried in 2 parts by weight refined paraffin distillate (150 SU viscosity of 100°F.) is added to the mixture. A nitrogen atmosphere (blanket) is maintained over the reaction mixture and stirring is continued while the reaction mixture is maintained at 170°F.± 1°F. for about 4 hours. The temperature is raised to 250°F. over a two hour period which serves to drive the reaction to completion.

The anti-foulant property imparted by the additive or additive combination was determined by adding it to liquid petroleum fractions and submitting the treated oils to degradation in the CFR Coker Test (ASTM Method D-1660) which is an industry test for measuring the fouling and coking tendencies of jet fuels. It has also been widely used with various modifications for measuring the fouling tendency of other hydrocarbon fractions. In accordance with this method, the filtered petroleum fraction under test is charged at a 6 lbs. per hour flow rate over an electrically heated preheater tube which heats the test fraction to the specified temperature. From the preheater section, the test sample is passed through a precision sintered stainless steel filter electrically heated to a specified temperature. The anti-foulant activity of the additive was determined basis its effectiveness to: (1) inhibit the buildup of deposits on the preheater tube (by comparison with the Base Fuel), and (2) prevent the agglomeration of insoluble degradation products which would otherwise precipitate from the fuel and become trapped by the filter, resulting in a significant pressure drop. In the tests discussed below, the CFR Coker was operated at temperatures somewhat higher than normal for testing jet fuels in order to increase the severity of the test. The resulting deposits were considerably heavier than would be obtained in a CFR Coker test on jet fuel and were therefore rated by the following scale:

Rating	Description of Deposits
A	None
B	½ to 1½ inches slight discoloration
C	1½ to 2 inches "Peacock" to light brown
D	2 to 2½ inches "Peacock" to light brown
E	2½ to 3 inches light brown to brown
F	3 to 3½ inches brown to dark brown
B	3 to 4 inches dark brown to black

In Table I below is set forth the anti-foulant results obtained with a kerosene base fuel. This fuel, designated Base Fuel A, had the following properties:

Gravity, °API		42.5
Gum, mg./100 ml.		1.0
Nitrogen, total p.p.m.		2.6
Sulfur, wt. %		0.031
Mercaptan Sulfur, g./l.		0.011
Distillation, ASTM, ° F.	IBP	361
	10%	392
	50%	426
	90%	474
	EP	506

The CFR Coker Test results reported are the pressure drop across the filter, P, in inches of Hg., the length of the test in minutes, and the relative amount of deposit on the tube.

TABLE I

Run	Base Fuel And Additive	Additive Dosage PTB	Stability at 420°/500° F. P,in.Hg./Time, mins./Tube		Deposit (F)
1	Base Fuel A	none	25.0	204	
2	Base Fuel plus Copolymer of Example 1	5	0	300	(A to B)
3	Base Fuel plus Copolymer of Example 1 N,N'-disalicylidene-1,2-propane diamine	4 1	0	300	(A to B)

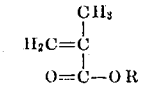
The non-additive containing Base Fuel had a very large pressure drop of 25.0 inches of mercury across the filter and the test had to be discontinued at 204 minutes. In contrast, the additive-containing fuel caused no pressure drop and the test was voluntarily stopped at 300 minutes. The amount of tube deposits for the additive-containing fuels, Runs 2 and 3, containing the copolymer of Example 1 and the additive combination of Example 1 with N,N'-disalicylidene-1,2-propane diamine, were from none to slight discoloration. In contrast the Base Fuel produced brown to dark brown deposits in a much shorter time on test. This test shows that the stability and deposit-forming tendency of the additive-containing fuels were outstandingly improved in comparison to the non-additive-containing Base Fuel. The anti-fouling method described is a very valuable and effective method for treating a wide range of petroleum feedstocks including naphthas, kerosene, gas oils, crude oil and similar liquid hydrocarbon feedstocks. The process is particularly useful in petroleum refining and petrochemical processes.

I claim:

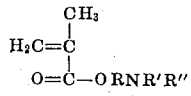
1. In the treatment of a hydrocarbon liquid at an elevated temperature wherein carbonaceous deposits are normally formed in said liquid and deposited on the processing equipment to foul same, the method of inhibiting fouling in said treatment which comprises incorporating in said hydrocarbon liquid an anti-fouling amount of an oil-soluble addition-type copolymer containing in combined form as its essential monomeric components copolymerizable ethylenically unsaturated compounds each containing only one polymerizable ethylenic linkage, at least one of which component is amine-free and contains from 4 to about 18 carbon atoms in an aliphatic hydrocarbon chain which in the polymer is not part of the main chain, one of the components as it exists in the polymer containing a basic aminonitrogen in the side chain, and one of the components containing a hydrocarbon-substituted-amide in the side chain, said copolymer containing from about 0.1 to 3.5 percent of said basic amino nitrogen and from about 0.05 to 4 percent of said component containing said amide.

2. A method according to claim 1 in which said hydrocarbon liquid contains from about 0.0005 to 0.5 weight percent of said copolymer.

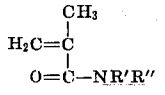
3. A method according to claim 1 in which said amine-free ethylenically unsaturated compound is represented by the formula:



in which R is an aliphatic hydrocarbon radical having from 1 to 18 carbons, said basic amino nitrogen-containing ethylenically unsaturated compound is represented by the formula:



in which R is an alkylene radical having from 2 to 4 carbon atoms and R' and R'' are hydrogen or an aliphatic hydrocarbon radical having from 1 to 8 carbon atoms, and said hydrocarbon-substituted amide compound is represented by the formula:



in which R' and R'' are hydrogen or an aliphatic hydrocarbon radical having from 1 to 18 carbon atoms.

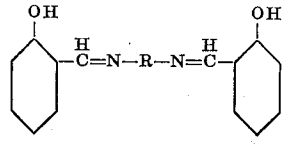
4. A method according to claim 1 in which said hydrocarbon liquid is kerosene.

5. A method according to claim 1 in which said hydrocarbon liquid is a naphtha.

6. A method according to claim 1 in which said hydrocarbon liquid is a gas oil.

7. A method according to claim 1 in which said hydrocarbon liquid is a crude oil.

8. A method according to claim 1 in which said hydrocarbon liquid being treated also contains an antifouling amount of an aldehyde-amine condensation product represented by the formula:



in which R is a divalent hydrocarbyl radical having from 2 to 4 carbon atoms.

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