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3,554,897

ANTIFOULANT ADDITIVE OF N-CONTAINING METHACRYLATE COPOLYMERS

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7 Claims

ABSTRACT OF THE DISCLOSURE

Treating method at 200 to 1200° F. to effect distillation, reforming, cracking, isomerization, hydrogenation, alkylation and/or polymerization involving addition of an oil-soluble, basic amino-nitrogen-containing addition-type copolymer to the hydrocarbon feed stream to inhibit fouling.

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, alkylation and polymerization of hydrocarbon fractions, such as naphthas, kerosene, gas oils and crude oils. The deposit-forming tendency of the oils 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 clean-up costs incurred when the deposits are removed from the equipment. To date, no completely satisfactory method has been discovered to prevent the buildup of deposits in petroleum process equipment.

A method has now been discovered which inhibits or substantially prevents the formation of deposits in petroleum refining equipment.

In accordance with this invention, there is provided a process whereby a liquid petroleum charge stock which is exposed to a high temperature and/or pressure in contact with a metal surface in refinery process equipment normally resulting in the formation of deposits thereon is first treated with an additive which inhibits or substantially prevents the formation of deposits in the treated stream and thereby prevents fouling of the process equipment. The material which has been found effective for this purpose is an oil-soluble basic amino-nitrogen-containing addition-type polymer of a plurality of polymerizable ethylenically unsaturated compounds. At least one of these ethylenically unsaturated compounds is amine-free and contains from 4 to about 18 carbon

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atoms in a predominantly straight chain aliphatic hydrocarbyl group which, in the polymer, is not part of the main polymer chain. At least one of the other ethylenically unsaturated compounds contains an amino nitrogen group which exists in the polymer as a basic amino nitrogen in the side chain. Said polymer contains from about 0.1 to 3.5 percent by weight of basic amino nitrogen.

The methacrylate esters are particularly suitable as both the amine-free ethylenically unsaturated component and the basic amino nitrogen containing component of the copolymer. Examples of the first class of esters are butyl methacrylate, lauryl methacrylate, stearyl methacrylate, decyl methacrylate - 2 - ethylhexyl methacrylate and mixtures of these methacrylate esters. Examples of the nitrogen-containing ethylenically unsaturated compounds include diethylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, phenyl aminomethyl methacrylate, butyl aminoethyl methacrylate, propyl aminoethyl methacrylate and the like.

Copolymers useful in the practice of the invention can be prepared by conventional bulk, solution or dispersant polymerization methods using known catalysts, such as benzoyl peroxide and azo compounds, such as alpha, alpha-azodiisobutyronitrile. Convenient solvents for the polymerization are high-boiling hydrocarbons, particularly those similar to the hydrocarbons in which the copolymers are to be used, such as kerosene. These polymerization processes are generally carried out in an inert atmosphere, for example, nitrogen or carbon dioxide at temperatures ranging from 30° C. to 150° C. depending on the catalyst used, and preferably at a temperature between 75° C. and 100° C. when alpha, alpha-azodiisobutyronitrile is used as the catalyst. It is important to carry the copolymerization substantially to completion so that no unpolymerized monomers remain and the proportions of each component in the final product are essentially those of the original monomer mixture.

Oil-soluble basic amino nitrogen-containing copolymer meeting the above description can be prepared from the copolymerization of n-octyl methacrylate with diethylaminoethyl methacrylate, lauryl methacrylate with diethylaminoethyl methacrylate, lauryl methacrylate with phenyl aminomethyl methacrylate, tridecyl methacrylate with diethylaminoethyl methacrylate and the like. The method of preparing the addition polymer useful in the process of the invention is set forth in U.S. 2,737,452.

The process of this invention involves adding a minor amount of the oil soluble, basic amino nitrogen-containing addition type copolymer to the liquid hydrocarbon being processed, the amount being effective to inhibit the formation and laydown of deposits in the process equipment. Depending on the nature of the hydrocarbon stream being processed, an effective deposit inhibiting amount of the additive will range from about 0.0005 to about 0.5 percent by weight of the feedstream. The preferred amount of the additive will generally be from about 0.001 to 0.05 weight percent of the additive, amounts corresponding to about 4 to about 130 p.t.b. (pounds of additive per thousand barrels of hydrocarbon).

The following example illustrates the preparation of an oil soluble, basic amino nitrogen-containing additive type copolymer.

Butyl methacrylate, 42 g., was charged to the resin kettle, 0.22 g. azobisisobutyronitrile was added, and the mixture stirred until it was all dissolved. The remainder of the monomer charge, 8 g. dimethylaminoethyl methacrylate, 106 g. lauryl methacrylate, and 44 g. stearyl meth-

acrylate, were added. The total monomer charge was 200 g. The solvent, a refined paraffin distillate of approximately 150 SU viscosity at 100° F., was weighed out, and the 286 g. were added to the resin kettle. The solution was purged with prepurified nitrogen gas with stirring for about ½ hour following which a nitrogen blanket was maintained over the reaction mixture. The reaction was continued at about 85° C. until a constant value in the refractive index indicated that the reaction was near completion. An additional 0.04 g. azobisisobutyronitrile was dissolved in 1 g. benzene and added dropwise to the solution. After 20 minutes, the pot temperature was raised to 100° C. and kept there until a constant value for the refractive index showed that the reaction was complete. This product was designated Additive A.

The antifoulant property imparted by the additive 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 hydrocarbon fractions at an elevated temperature. 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 as passed through a precision sintered stainless steel filter electrically heated to a specified temperature. The antifoulant 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 Table I below is set forth the antifoulant results obtained with a gasoline. The base fuel in this test designated Base Fuel A, was a heavy straight run gasoline which had the following properties:

Gravity, ° API	54.5
Color, Saybolt	30
Sulfur, wt. percent	0.008
Mercaptan sulfur, g./l.	0.004
Distillation, ASTM, ° F.:	
IBP	236
10%	247
50%	266
90%	299
EP	320

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

TABLE I

Base fuel and additive	Additive dosage, p.t.b.	Stability at 425°/500° F.		
		ΔP , in. Hg.	Time, mins.	Tube deposit
Base fuel A	none	20.8	300	Heavy amount of brown deposit.
Base fuel plus additive A.	5	0	300	Light amount of brown deposit.

The nonadditive containing Base Fuel had a very large pressure drop of 20.8 inches of mercury across the filter as compared to no pressure drop with the additive-containing fuel. The amount of tube deposit for the additive-containing fuel was also very substantially less than the amount of tube deposit for the Base Fuel. This test shows that the stability and deposit-forming tendency of the additive-containing fuel was very substantially improved in sharp contrast to the results obtained with the non-additive Base Fuel.

The antifouling properties of a kerosene containing the additive of the invention was also determined in the above-

described CFR Coker Test. The test fuel in this test was a kerosene, designated Base Fuel B, which had the following properties:

Gravity, ° API	43.4
Sulfur, wt. percent	0.071
Mercaptan sulfur, g./l.	0.112
Gum, potential, mg./100 ml.	4
Nitrogen, total, p.p.m.	5
Organic acidity, mg. KOH/g.	0.080
Copper content, p.p.b.	132
Water reaction	1B
Water Separometer Index Modified	80
Distillation, ASTM, ° F.:	
IBP	324
10%	361
50%	416
90%	485
EP	521

The results of the CFR Coker Test using Base Fuel B are given in Table II.

TABLE II

Base fuel and additive	Additive dosage, p.t.b.	Stability at 425°/500° F.		
		ΔP , in. Hg.	Time, mins.	Tube deposit
Base Fuel B	none	25.0	120	Heavy amount of brown to dark brown deposit.
Base Fuel B plus Additive A.	5	0.3	300	Light amount of dark brown deposit.

The foregoing test demonstrates the remarkable effectiveness of the instant anti-fouling method. The formation of deposits in the Base Fuel B kerosene caused the maximum pressure drop permitted in this test of 25 inches of mercury across the filter at which time the test was terminated. Termination of the test came after 120 minutes. The tube had a heavy, brown deposit. In contrast, the additive-containing kerosene with 5 p.t.b. of Additive A caused an insignificant pressure drop across the filter, namely a drop of 0.3 inch of mercury, after the full test period of 300 minutes. The amount of tube deposit for this additive-containing fuel was also much less than that of the nonadditive fuel.

It is evident that a very valuable and effective anti-fouling method has been discovered which is generally suitable in the processing of a variety of petroleum feed-streams.

Obviously, many modifications and variations of the invention, as hereinafter set forth, may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In a process for treating a hydrocarbon liquid at an elevated temperature in the range from about 200° F. to 1200° F. to effect distillation, reforming, cracking, isomerization, hydrogenation, alkylation or polymerization wherein carbonaceous deposits are normally formed in said liquid and deposited on the processing equipment, the improvement which comprises incorporating in said hydrocarbon liquid an antifouling amount of 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% by weight of basic amino-nitrogen and said copolymer having an inherent viscosity of

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0.1 to 3.0 as determined at 0.1% weight-volume concentration in benzene at 25° C.

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

3. A method according to claim 1 in which said hydrocarbon liquid is a kerosene distillate.

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

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

6. A method according to claim 1 in which said alkacrylic ester is a methacrylate ester and said basic amino nitrogen-containing component is a dialkylamino-alkyl methacrylate.

7. A method according to claim 1 in which the components of said copolymer are a mixture of alkylmeth-

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acrylates in which the alkyl radical has from 4 to 18 carbon atoms and dimethylaminoethyl methacrylate.

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