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REFINERY PROCESS STREAM ANTI-FOULANT

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This invention relates to the treatment of refinery feed stream hydrocarbons and more particularly pertains to the treatment of hydrocarbon feed streams which have a tendency to form equipment-fouling deposits when heated to a temperature above about 300° F. before subjecting the feed streams to refinery processes including separation processes, upgrading processes and hydrocarbon conversion processes. More specifically, the invention relates to a method for inhibiting, to a substantial extent, the propensity of said hydrocarbon feed streams to form gums, sediment and similar deposit formers during and after preheating.

In many refinery processes hydrocarbon streams both unrefined and partially refined hydrocarbons are preheated before being subjected to liquid and/or vapor phase processing. For example, crude petroleum is preheated by indirect heat exchange with product stream and then subjected to final preheating in a furnace before charging to a pipe still for the separation and recovery of various petroleum fractions. Likewise, topped crude is preheated before being subjected to vacuum distillation for the separation and recovery of hydrocarbon fractions of said topped crude. Other unrefined liquid hydrocarbon streams such as natural gas liquids are also preheated before being subjected to refinery processes. Partially refined liquid hydrocarbons such as virgin gas oil, gas oil from vis-breaking, gas oil from coking, light gas oil, virgin naphtha, light and heavy naphtha fractions from pipe still distillation, paraffin distillates, cycle oil from catalytic cracking, coker naphtha, and other such partially refined liquid hydrocarbons are preheated before being subjected to such hydrocarbon conversion processes as thermal cracking, catalytic cracking, thermal reforming, catalytic reforming and other conversion processes. In addition, preheating is employed before liquid hydrocarbon feed streams are subjected to hydrocarbon enrichment or upgrading processes as absorption enrichment of lean oil and/or stripping processes. For these hydrocarbon separation processes, hydrocarbon enrichment processes and hydrocarbon conversion processes, the unrefined and partially refined liquid hydrocarbon feeds are preheated to temperatures over a wide range depending on the temperature requirements of further processing and depending upon the physical phase involved in the further processing such as liquid phase, vapor phase or a combination of liquid and vapor phases. In general, the various preheating temperatures are within the range of 300 to 1500° F.

It is recognized in petroleum refining that the various refinery feed streams would present fewer problems with respect to fouling of heating surfaces and fouling of process stream filters, generally in-line filters, provided that these feed streams had not been contacted with oxygen, especially air. Contact with air might be avoided when petroleum fractions and process hydrocarbon fractions are immediately charged to further separation upgrading and/or conversion processes. To do so would require all refinery operations to be conducted on a totally continuous basis. Such total continuous refining is not feasible and various liquid hydrocarbon streams must be held in storage before they are further used in other refinery processes. Even continuous refinery operation would not prevent air contact with crude petroleum or other crude hydrocarbons such as natural gas liquids, for

these crude hydrocarbons cannot be produced and transported to refineries without contact with air. Since these air contacted sources of crude hydrocarbons do have the tendency to form gums and/or sediments upon preheating for use in refinery processes even in a totally continuous refinery operation, they still present the problems of fouling heating surfaces and in-line filters.

Blanketing of unrefined and partially refined liquid hydrocarbons with inert gas such as nitrogen has been proposed to partially alleviate the problems encountered by fouling of heating surfaces of heat exchangers during preheating steps and the after-fouling by preheated liquid hydrocarbons of filtering devices installed to prevent undesirable suspended gums, sediments, etc. from entering refinery processes. Certain chemical compounds and mixtures of chemical compounds have been proposed as additives for the unrefined and partially refined liquid hydrocarbons as anti-foulant additives to reduce the tendency for gum and/or sediment formation during preheating in heat exchangers beyond that fouling reduction achieved by inert gas blanketing of stored liquid hydrocarbons. Most of the commercially available anti-foulants are propriety compositions sold under various trade names, trademarks and grade marks. Consequently, their precise chemical composition cannot be readily ascertained.

We have now discovered a class of new anti-foulants which can be used in small amounts as additives for unrefined and partially refined liquid hydrocarbons which have a propensity for depositing gums and/or sediments upon heating to a temperature above 300° F., in the range of 300 to 1500° F., which anti-foulant additives prevent, to a substantial extent, the fouling of heat exchange surfaces and process stream filters by the gums and/or sediments which would normally be formed. The new class of anti-foulants for use in said unrefined and partially refined liquid hydrocarbons to be preheated is an oil-soluble additive complex obtained by reacting a phosphorous sulfide, e.g. phosphorous pentasulfide, with a normally non-gaseous hydrocarbon, as hereinafter described, and hydrolyzing the resultant reaction product.

In accordance with the present invention there is provided a method of preventing the deposition of solids at temperatures of from 300 to 1500° F. by liquid hydrocarbons which have a propensity for depositing gums and sediments when heated to such temperatures which comprises incorporating in said liquid hydrocarbons from 5 to 250 p.p.m. of a hydrolyzed phosphorous sulfide-hydrocarbon reaction product.

In the preparation of the phosphorous sulfide-hydrocarbon reaction products, the hydrocarbon is reacted with a phosphorous sulfide, such as P_2S_3, P_4S_3, P_4S_7 or other phosphorous sulfides, and preferably phosphorous pentasulfide, P_2S_5.

The hydrocarbon constituent of this reaction is suitably a normally non-gaseous hydrocarbon such as is described in detail in U.S. 2,316,080, 2,316,082, and 2,316,088, each issued to Loane et al. on April 6, 1943. While the hydrocarbon constituent of this reaction can be any of the type hereinafter described, it is preferably a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefinic hydrocarbons or isomono-olefinic hydrocarbons, such as propylene, butylenes, and amylenes or the copolymers obtained by the polymerization of hydrocarbon mixtures containing iso-mono-olefins and mono-olefins or mixtures of olefins in the presence of a catalyst, such as sulfuric acid, phosphoric acid, boron fluoride, aluminum choloride or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and iso-mono-olefin polymers having molecular weights ranging from about 150 to about 50,000 or more, and preferably

from about 300 to about 10,000. Such polymers can be obtained, for example, by the polymerization in the liquid phase of a hydrocarbon mixture containing mono-olefins and isomono-olefins such as butylene and isobutylene at a temperature of from about −80° F. to about 100° F. in the presence of a metal halide catalyst of the Friedel-Crafts types such as, for example, boron fluoride, aluminum chloride, and the like. In the preparation of these polymers we may employ, for example, a hydrocarbon mixture containing isobutylene, butylenes and butanes recovered from petroleum gases, especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline.

Essentially paraffinic hydrocarbons such as bright stock residuums, lubricating oil distillates, petrolatums, or paraffin waxes, may be used. There can also be employed the condensation products of any of the foregoing hydrocarbons, usually through first halogenating the hydrocarbons, with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride, and the like.

Other preferred olefins suitable for the preparation of the herein described phosphorus sulfide reaction products are olefins having at least 20 carbon atoms in the molecule of which from about 13 carbon atoms to about 18 carbon atoms, and preferably at least 15 carbon atoms, are in a long chain. Such olefins can be obtained by the dehydrogenation of paraffins, such as by the cracking of paraffin waxes or by the dehalogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

Also contemplated within the scope of the present invention are the reaction products of a phosphorus sulfide with an aromatic hydrocarbon, such as for example, benzene, naphthalene, toluene, xylene, diphenyl and the like or with an alkylated aromatic hydrocarbon, such as for example, benzene having an alkyl substituent having at least four carbon atoms, and preferably at least eight carbon atoms, such as long chain paraffin wax.

The phosphorus sulfide-hydrocarbon reaction product is prepared by reacting the phosphorus sulfide, e.g. P_2S_5, with the hydrocarbon at a temperature of from about 150° F. to about 600° F., preferably from about 300° F. to about 500° F., using from 1% to about 50%, preferably from about 5% to about 25% of phosphorus sulfide; the reaction is carried out in from about one to about ten hours. It is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification is necessary; however, an excess of the phosphorus sulfide can be used, and the unreacted material separated by filtration. It is advantageous to maintain a non-oxidizing atmosphere, for example an atmosphere of nitrogen, in the reaction vessel. The reaction product obtained is then hydrolyzed at a temperature of from about 200° F. to about 500° F., preferably at a temperature of about 300° F.–400° F. by suitable means, such as for example, by introducing steam through the reaction mass. The hydrolyzed product, containing inorganic phosphorus acids formed during the hydrolysis, can be used as such or it can be substantially freed of the inorganic phosphorus acids by contacting with an adsorbent material such as Attapulgus clay, fuller's earth and the like at a temperature of 100° F.–500° F. as fully described and claimed in U.S. 2,688,612, issued to R. Watson, Sept. 7, 1954, or by extraction with phenol or an alkanol of 1 to 5 carbon atoms in admixture with water as described and claimed in Lemmon et al. U.S. Patent No. 2,843,579.

The following specific examples illustrate the preparation of the herein described hydrolyzed phosphorous sulfide-hydrocarbon reaction product. It is to be understood that the examples are for the purpose of illustration only and are not to be regarded as a limitation of the present invention.

EXAMPLE I

A butylene polymer having a molecular weight of about 780 was reacted with 15.5 wt. percent P_2S_5 at about 450° F. for about 5.5 hours, and the product hydrolyzed by steaming at 300° F. for about 5½ hours. The resultant hydrolyzed product was diluted to 50% by volume with kerosene to produce an antifoulant additive having as the active ingredient hydrolyzed phosphorous sulfide-hydrocarbon reaction product.

EXAMPLE II

A polybutene having an average molecular weight of about 780 and a Saybolt Universal viscosity at 210° F. of about 1,000 seconds was reacted with 15.5 wt. percent P_2S_5 at 450° F. for about 4.5 hours, and the product hydrolyzed by steaming at 300° F. for about 5½ hours. The resultant hydrolyzed reaction product contained 4.4 wt. percent phosphorous and 2.9 wt. percent sulfur.

The herein described hydrolyzed phosphorous sulfide-hydrocarbon reaction product can be used as an antifoulant in amounts from about 5 to 250 parts per million parts of oil by weight (p.p.m.), preferably in amounts of from about 10 to about 100 p.p.m.

The antifoulant property of the hydrolyzed phosphorous sulfide-hydrocarbon reaction product is demonstrated by data in Table 1, below, which data were obtained in a Coker Model O2FC. A detailed description of the test equipment and procedure is given in ASTM designation D–1660–61T. Briefly, 10 gallons of the test oil is prefiltered through filter paper. The test oil is then pumped consecutively through an in-line filter, a rotometer and a preheater. In the preheater the test oil flows through an annulus enclosing a polished aluminum or carbon steel tube. An electric heating element inside the tube heats the oil to a controlled predetermined temperature. Hot oil from the preheater annulus can then be heated to a higher temperature before passing through a precision sintered steel filter. Hot oil from the filter is then cooled in a water-cooled heat exchanger. The oil then flows into a container on a scale for flow rate determination. An operating pressure of 150 p.s.i.g. is normally used. An oil flow rate of 6 lbs. per hour was employed during the tests.

During the coker run the filter presure drop was recorded every 10 minutes. The pressure drop across the filter varied exponentially with time and a plot of the logarithm of the filter presure drop versus time is a straight line. Hence, fouling tendency is compared by a comparison of the slope of the straight lines obtained from such a plot during coker runs on test oils with and without the hydrolyzed phosphorous sulfide-hydrocarbon reaction product antifoulant additive. The slope of the presure drop lines is calculated as $(\log \Delta P_2 - \log \Delta P_1)/(T_2 - T_1)$, where ΔP and T represent filter pressure drop and time, respectively, and two different time ΔP measurements during the coker run.

Comparison of the slopes for the various lines has been made easier by assigning an arbitrary "Fouling Index" of 1 to the slope of a standard or base line and comparing all other slopes to it. The pressure drop versus time line obtained during a coker run employing virgin naphtha as the test oil, which line had a slope of 0.0035, was used as the standard and assigned a Fouling Index of 1. Hence, a test oil having a Fouling Index of 2 means that the slope of a plot of the log of pressure drop versus time is twice as great as that for the standard naphtha and the fouling tendency or Fouling Index is twice as great. Experience has shown that there is a direct relationship between Fouling Index and fouling experienced during commercial operations.

Various oils were subjected to the above coker test with and without antifoulant additive incorporated therein. The antifoulant additive used during these comparative tests was prepared according to Example I above. The antifoulant additive concentrations given are the concentrations of a mixture of the hydrolyzed phosphorous sulfide-hydrocarbon reaction product and an equal volume of

kerosene as in Example I. The data obtained during these tests are shown in Table 1.

TABLE 1.—RESULTS OF COMPARATIVE COKER TESTS

Test	Test Oil	Fouling index of test oil	Anti-foulant conc., p.p.m.	Fouling index with anti-foulant
A	Desalted crude oil	2.7	40	0.5
B	50 vol. percent desalted crude oil, 50 vol. percent kerosene.	7.8	40	1.0
C	10 vol. percent desalted crude oil, 90 vol. percent kerosene.	2.7	40	0.5
D	Gas oil feed to catalytic cracker.	3.7	40	1.8
E	50 vol. percent heavy virgin gas oil, 50 vol. percent kerosene.	12.4	40	0.6
F	Aerated kerosene	9.1	20	<0.1
			40	0.2
G	50 vol. percent desalted crude oil, 50 vol. percent kerosene.	12.3	80	2.5
			120	0.8
H	Desulfurizer naphtha feed	4.3	30	0.0
			40	0.0

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as come within the spirit of the appended claims.

What is claimed is:

1. A method of preventing the deposition of solids in petroleum refinery processing equipment at temperatures between about 300° F. and about 1500° F. by unrefined and partially refined liquid hydrocarbons which have a propensity for depositing gums and sediments when heated to said temperatures, which method comprises incorporating in said liquid hydrocarbons which are present in said equipment, a hydrolyzed phosphorus sulfide-hydrocarbon reaction product.

2. A method of preventing in petroleum refinery processing equipment the fouling of heat exchange surfaces which contact unrefined and partially refined liquid hydrocarbon fractions having a propensity for depositing gums and sediments on said heat exchange surfaces, which method comprises adding to said liquid hydrocarbon fractions before contact with said heat exchange surfaces from 5 to 250 p.p.m. of a hydrolyzed prosphorus sulfide-hydrocarbon reaction product.

3. The method of claim **1** wherein said liquid hydrocarbons comprise a petroleum hydrocarbon fraction from catalytic cracking to be subjected to hydrocarbon conversion for gasoline blending stock.

4. The method of claim **1** wherein said liquid hydrocarbons comprise a partially refined distillate fuel feed for hydrodesulfurization.

5. The method of claim **1** wherein said liquid hydrocarbons comprise a naphtha feed for catalytic reforming.

6. The method of claim **1** wherein said liquid hydrocarbons comprise a gas oil feed for catalytic cracking.

7. The method of claim **1** wherein said liquid hydrocarbons are desalted crude petroleum.

8. The method of claim **1** wherein said liquid hydrocarbons are produced during coking of a heavy petroleum fraction.

9. The method of claim **1** wherein said hydrolyzed reaction product is present in an amount from 5 to 250 p.p.m. and said hydrolyzed reaction product is prepared by reacting phosphorus sulfide with non-gaseous hydrocarbons at a temperature between about 150° F. and about 600° F., using from 1% to about 50% of phosphorus sulfide and a reaction time in the range of about one to ten hours, and hydrolyzing the product of the reaction at a temperature between about 200° F. and about 500° F.

10. The method of claim **9** wherein said phosphorus sulfide is phosphorus pentasulfide.

References Cited

UNITED STATES PATENTS

2,849,398	8/1958	Moody et al.	252—32.7
3,017,357	1/1962	Cyba	252—32.5

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