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PROCESS OF HEAT TRANSFER

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4 Claims. (Cl. 208—48)

The present invention relates to improvements in the intermediate stages of refining petroleum hydrocarbons. The invention is concerned specifically with chemical additives to prevent loss or impairment of heat transfer in refinery processing equipment in which normally-liquid charge stocks are used.

A purpose of the invention is to introduce into a hydrocarbon which may consist of naphthalene, gas oil, crude oil, residuum, light distillate, gasoline or a mixture thereof, heated at a temperature of 200 to 1100° F., from 1 to 200 parts per million by volume of an improved heat transfer additive.

A further purpose is to improve the heat transfer in petroleum refining by adding to the petroleum undergoing refining a reaction product of alkyl or alkenyl substituted succinic acid or succinic anhydride having from 30 to 200 carbon atoms, inclusive, in the alkyl or alkenyl group, and having from 1 to 5 repetitions of the molecule in a polymer, with propylene diamine having the formula:

$$H_2N-CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-NH_2$$

the proportions of propylene diamine varying between one-half and 2 equivalents per equivalent of substituted succinic acid or succinic anhydride.

A further purpose is to employ as a heat transfer additive a substituted succinic acid or succinic anhydride having a molecular weight between 600 and 1,000.

Further purposes appear in the specification and in the claims.

One of the principal problems encountered in the refining of various petroleum charge stocks is the formation of solid deposits on the metal surfaces of the processing equipment. As a result of such deposits, the heat transfer through these surfaces gradually decreases during operation of the equipment until it would be necessary to shut down the equipment for cleaning unless special precautions were taken. This phenomenon is particularly severe in refinery operations where the charge stock flows through various types of heat processing equipment, such as pipes, heat exchangers, furnaces, stills, etc. Such equipment for purposes of simplification is referred to elsewhere herein as a conductor or metal conductor. The types of mechanical equipment in which the problem is most commonly encountered are furnaces, heat exchangers, reboilers and condensers.

The charge stocks which are most commonly encountered in the intermediate refinery equipment are naphthas, gas oils and crude oils. These various charge stocks are heated during refinery processing to temperatures which range between 200° F. and 1100° F. It is at these elevated temperatures that the heat transfer coefficient between the oil and the conductors becomes seriously impaired by the formation of the deposits.

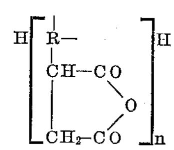
The composition of the solid deposits varies and would appear to be a mixture of polymerization products and carbonaceous solid particles. These deposits are not readily solubilized by organic solvents.

When the phenomenon of fouling first became apparent, it was believed that difficulty could be successfully overcome by using antioxidants or dispersants. These additives were tried and were not effective.

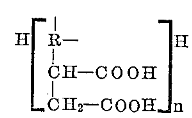
The deposits are objectionable in two ways. They not only impede the flow of the oil streams through the heat transfer equipment, but even more serious, they greatly reduce the coefficient of heat transfer across the heat transfer surfaces. There is an almost linear relationship between the weight of the deposits produced in the conductor and the percentage drop in heat transfer coefficient. There is, therefore, an important need for a chemical additive which when supplied at relatively low dosage would prevent loss in heat transfer coefficient and avoid any down time incident to taking equipment out of service for cleaning.

The present invention solves this problem by applying a chemical which is admixed with the charge stock before it goes through the heat tarnsfer equipment. This additive is capable of maintaining a high heat tranfer coefficient in the conductor through forming a stable chemisorbed film on the metal surface of the conductor. The product is an alkyl or alkenyl substituted succinimide.

The additive employed in the present invention is the result of reacting a substituted succinic anhydride having the following formula:



or a substituted succinic acid having the following formula:



in which R is an alkyl or alkenyl radical having from 30 to 200 carbon atoms in the carbon chain, and n is an integer between 1 and 5, inclusive, with propylene diamine having the formula:

$$H_2N-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-NH_2$$

In the above reaction, from one-half to 2 chemical equivalents of propylene diamine are used for one chemical equivalent of succinic compound.

British Patent No. 922,831, published April 3, 1963, for Metal-Free Lubricant Additives, describes the syntheses of compounds similar to the additive of the present invention. The alkyl succinic anhydride discussed in this reference was prepared from a chlorinated polyisobutylene and maleic anhydride. Either a chlorinated or nonchlorinated polyisobutylene may be used to prepare additives for the purposes of the present invention.

The alkyl or alkenyl radicals (mono or polyunsaturated) substituted in the succinic acid or succinic anhydride are commonly obtained from polyolefins such as polyethylene, polypropylene, polyisobutylene or copolymers of styrene or any other alkenyl groups capable of forming copolymers with maleic anhydride or maleic acid. These substituent groups are large, having between 30 and 200 carbon atoms in the molecule and preferably between 30 and 100 carbon atoms in the molecule, both inclusive. The reaction involves thermal condensation of these reactants at temperatures between 200 and 300° C.

The most commonly used sources of these substantially aliphatic hydrocarbon substituents are the polyolefins. Examples are polyethylene, polypropylene, polyisobutylene, and so on up the series. A particularly desirable polyolefin for this use is polyisobutylene present in polymers having a molecular weight between 600 and 1,000 inclusive.

In my copending application Serial No. 434,618, filed February 23, 1965, for Process of Heat Transfer, I describe and claim a process by which condensation products between alkyl or alkenyl substituted succinic acids or succinic anhydrides and certain straight carbon chain polyamines give protection against loss of heat transfer inversely proportional to the weight of fouling products deposited on the heat transfer surface.

In the present application I describe and claim a process of improving heat transfer by employing as additives certain condensation products of alkyl or alkenyl substituted succinic acids or succinic anhydrides with propylene diamine having the following structural formula:

$$H_2N-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$$

These compounds which as shown above having a branched carbon chain, function in a manner entirely different from those referred to in my copending application. They offer protection against loss of heat transfer entirely independent of the weight of fouling products deposited on the heat transfer surface. Furthermore, the nature of the fouling deposit obtained with an additive of the present invention is entirely different from that obtained with additives of my copending application above referred to. In the absence of an antifouling additive, the typical deposit produced on the heat transfer surfaces by the hydrocarbon consists of layers, the innermost of which is dense and coke-like and the outer layers of which are sticky semi-fluid masses. The fouling deposit obtained, however, on heat transfer surfaces when additives of the present invention are used are usually loose and consist of a thin layer which is coke-like in nature. The sticky polymeric outer layer is not present at all.

EXAMPLE 1

A representative compound of the present invention was prepared as follows:

A polyisobutenyl succinic anhydride was prepared by reacting polyisobutylene with maleic anhydride at 250° C. The polyisobutenyl radical in this case had an average molecular weight of 889 and the resulting alkenyl succinic anhydride had an acid number of 94 which corresponded to an equivalent weight of 596. To a mixture of 40 grams (0.067 equivalent) of this polyisobutenyl succinic anhydride and 15 milliliters of xylene, there was added at room temperature 2.24 grams of propylene diamine. The addition was made slowly, and an initial exothermic reaction caused the temperature to rise to 60° C. After this reaction ceased, the mixture was refluxed at 100° C. for about 20 minutes and then a water xylene azeotrope distilled from the mixture. When no more water would distill, the mixture was heated to 180° C. under atmospheric pressure. The residue was diluted with 50% xylene.

EXAMPLE 2

The reaction of Example 1 was carried out except that diethylene triamine was used instead of propylene diamine.

EXAMPLE 3

The reaction of Example 1 was carried out, but using a polyisobutenyl succinic anhydride compound having a molecular weight of 640.

EXAMPLE 4

The procedure of Example 1 was carried out by using a polyisobutenyl succinic anhydride compound having a molecular weight of 494.

It has been noted that at least one-half of a chemical equivalent of the amine should be used per chemical equivalent of substituted succinic acid or succinic anhydride, and it is preferable to use 1:1 proportions. It is not desirable to use more than 2 equivalents of polyamine per equivalent of succinic compound.

The additives of the invention are miscible in all proportions with the normally liquid hydrocarbons which are being refined.

The amount of the additive required to prevent reduction in heat transfer will depend on several factors, such as the design of the process equipment, the type and nature of the hydrocarbon charge stock, the operating pressures and temperatures, the flow rates, and the extent of inhibition of loss of heat transfer which is desired. It is, therefore, impossible to state any rigid rule for estimating the amount of an additive that will be needed. However, the amounts of the materials required in the application of the present invention are very small. For many purposes, amounts of the order of 0.5 pint per 1,000 barrels to 1 pint per 1,000 barrels are sufficient. In general, quantities greater than 17 gallons per 1,000 barrels will seldom be required. Stated in terms of parts per million by volume, it is belived that the minimum feed of the additive will be 1 part per million and the maximum 200 parts per million.

Although the products of the invention are notably effective in the prevention of heat transfer reduction, it is frequently convenient to use them with other types of additives such as metal deactivators, oxidation inhibitors and the like. The additive of the invention remains preferably with the liquid phase of the charge stock during the various stages of refining. For example, if a gas oil is subjected to a catalytic process, the additive of the invention does not carry over to any extent into the finished product, but will remain behind in the residue and nonconverted components of the liquid.

The additive of the invention may be added to the charge stock at any point in the process where protection is desired and will carry along and provide protection until such time as the product is converted to a different chemical compound or species. Thus, when a crude stock is passed through a heat exchanger to a thermal distillation unit to remove lighter fractions, the additive may be added just prior to the heat exchanger section of the operation and will afford improved heat transfer capabilities to the heat exchanger section and other heat transfer surfaces of the distillation or fractionation unit.

Evaluation

The test apparatus used to make comparative evaluations of refinery stream heat transfer efficacy consists of a variable injection pump, connected to a test heat exchanger, and a double-pipe water cooled heat exchanger connected in series. The test heat exchanger consists of a steel specimen tube in which an electrical heating mantle is incorporated. The fluid being tested flows single-pass through the tube for 20 hours. The oil temperature at the inlet and outlet of the heat exchanger tube and the wall temperature at the same points are recorded continually.

The fouling of the tube is determined by the change in heat transfer coefficient during the test after equilibrium has been attained. This coefficient is determined from the following equation:

$$Q=UA\Delta t$$

where

Q=heat input of the oil in B.t.u.'s per hour,

U=heat transfer coefficient in B.t.u. per hour per ft.^{2} per °F.,

A=area of heat transfer surface based on the internal surface area of the heat exchanger tube,

Δt=difference between the oil temperature and the wall temperature in °F.

The results of the tests are reported in percent heat transfer protection according to the following equation:

$$\text{Percent } HTP=100\frac{U^{F'}U^{*}-U^{F}U^{*'}}{U^{F'}(U^{*}-U^{F})}$$

where

U^{*}=average overall heat transfer coefficient for clean specimen in a control run,

$U^{*'}$=average overall transfer coefficient for clean specimen when additive has been added,

U^{F}=average overall heat transfer coefficient for the fouled specimen in a control run,

$U^{F'}$=average overall heat transfer coefficient for the fouled specimen when additive has been added.

Another method of evaluating the data from the testing of the additives is based on the reduction in the weight of fouling product. The percent inhibition of fouling based on the weight of fouling product (percent FI_w) is calculated as follows:

$$\text{Percent } FI_w=100\frac{\alpha-(W^{f}-W^{o})}{\alpha}$$

where

α=weight of fouling product deposited in the absence of an additive,

W^{f}=weight of fouling product deposited in the presence of an additive plus weight of test specimen,

W^{o}=weight of test specimen.

In the case of most additives the percent of heat transfer protection (percent TP) based on the heat transfer coefficients is proportional to the percent FI_w based on the weight of fouling product produced. In the case of the additive of the present invention, however, there is no correlation between the two factors. Very unexpectedly, the additive of the present invention gives superior heat transfer compared to other additives even when the other additives permit a smaller weight of fouling product to be formed. It is believed that this phenomenon is attributable to a change made in the nature of the fouling product in the present invention. Thus, the fouling product of the present invention even though present in greater thickness permits greater heat transfer than does a smaller weight of fouling product produced with other additives.

The amount of additive required to prevent reduction in heat transfer effectiveness will depend on several factors such as the design of the process equipment, the type and nature of the hydrocarbon charge stock, the operating pressures and temperatures, the flow rates, and the extent of inhibition of heat transfer reduction which is desired. It is, therefore, not possible to state rigid rules for estimating the amount of additive which will be employed in every instance. However, it can be stated that the amount of additive will be very small. For many purposes, amounts of additive of the order of 0.5 to 1 pint per 1,000 barrels are sufficient. In general, it can be stated that quantities greater than 17 gallons per 1,000 barrels are seldom required. Stated in terms of parts per million by volume, it is believed that the minimum feed of the additive will be 1 part per million and the maximum 200 parts per million.

Table 1 summarizes the results obtained using the additive of the present invention as compared with other additives.

TABLE 1

Additive	Percent Fouling Inhibition	Percent Heat Transfer Protection
1. Reaction product of Example 1, propylene diamine reacted with an alkyl succinic anhydride in which the polyisobutyl had a molecular weight of 889	55.3	100
2. Reaction product of Example 2	84.2	78
3. The salt of dodecylbenzene sulfonate and a C_{12} to C_{15} alkyl amine	58.5	57.3
4. An ethoxylated alkyl amino trimethylamine in which the alkyl group is C_{18} and having 2 ethoxyl groups per molecule	69.2	62.2
5. The reaction product of Example 3 in which the alkyl succinic anhydride has a molecular weight of 640	63.8	95.3
6. The reaction product of Example 4 in which the alkyl succinic anhydride has a molecular weight of 494	48.0	56.0

Tests 3 and 4 in Table 1 are controls showing other products which have been used as heat transfer additives. It will be noted that the products of the present invention compare very favorably with the controls and in some cases show considerable superiority. It is also evident that the propylene diamine derivative of the present invention gives optimum heat transfer regardless of the weight of fouling product deposited on the tube surface.

It is also apparent from Table 1 that the products of the present invention differ markedly in their properties depending on molecular weight. The data shown in Test 6 of Table 1 where the molecular weight was 494 indicates much lower heat transfer protection than when higher molecular weights were used, as in the data reported on Tests 1 and 5.

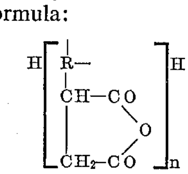
The propylene diamine derivative of the present invention has an unusual property in that it is soluble in light hydrocarbon such as pentane, butane and propane. Although the present invention applies to normally liquid hydrocarbons, there are some applications were light hydrocarbon solubility is desirable.

In view of my invention and disclosure, variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying the process shown, and I, therefore, claim all such insofar as they fall within the reasonable spirit and scope of my claims.

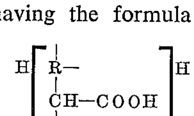
Having thus described my invention what I claim as new and desire to secure by Letters Patent is:

1. A process for preventing heat transfer reduction in a metal conductor, through which passes a hydrocarbon of the group consisting of naphthas, gas oils, crude oils, residuum, light distillate, gasoline or mixtures thereof, at a temperature between 200 and 1100° F., which comprises adding to said hydrocarbon chain group between 1 and 200 parts per million by volume of a reaction product of

(a) a member of the group consisting of alkyl substituted and alkenyl substituted succinic anhydrides having the formula:



and alkyl substituted and alkenyl substituted succinic acids having the formula:



wherein n is an integer between 1 and 5 inclusive, and R is a group of the class consisting of alkyl and alkenyl groups having between 30 and 200 carbon atoms in the carbon chain; and

(b) propylene diamine of the formula:

$$H_2N-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$$

the proportions of propylene diamine varying from one-half of 2 equivalents per equivalent of succinic compound.

2. A process of claim **1**, in which R is between 30 and 100 carbon atoms inclusive.

3. A process of claim **1**, in which the molecular weight of the succinic compound is between 600 and 1,000 inclusive.

4. A process of claim **1**, in which the succinic compound and the propylene diamine are reacted in equal proportions by weight.

No references cited.

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