United States Patent Office

3,271,295

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3,271,295

PROCESS OF HEAT TRANSFER

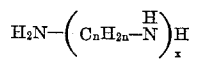
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10 Claims. (Cl. 208—48)

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 such as naphthalene, gas oil, crude oil, residuum, light distillate, gasoline, or mixtures 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 an 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 a polyamine having a formula



where n is an integer varying from 2 to 10 inclusive, x is an integer varying from 1 to 10 inclusive, and C_nH_{2n} is a straight chain hydrocarbon group, the proportions of polyamine varying from ½ to 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 of 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.

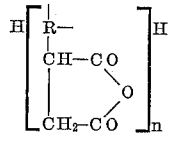
The composition of the solid deposits varies and would appear to be a mixture of polymerization products and carbonaceous solid particles. These deposits are not readily solubilized by organic solvents.

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

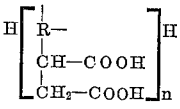
The deposits are objectionable in two ways. They not only impede the flow of the oil streams through the heat transfer equipment, but even more serious, they greatly reduce the coefficient of heat transfer across the heat transfer surfaces. There is an almost linear relationship between the weight of 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 transfer equipment. This additive is capable of maintaining a high heat transfer coefficiennt in the conductor by forming a stable chemisorbed film on the metal surface of the conductor. The additive is an alkyl or alkenyl substituted succinimide.

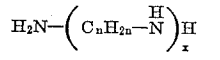
The additive employed in the present invention is the result of reacting a substituted succinic anhydride having the following formula:



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 a polyamine of the formula:



in which

n is an integer between 2 and 10 inclusive,
x is an integer between 1 and 10 inclusive, and
C_nH_{2n} is a straight chain hydrocarbon group.

In the above reaction, from ½ to 2 chemical equivalents of polyamine are used for 1 chemical equivalent of succinic compound.

The synthesis of compounds used in the present application is described in British Patent 922,831, published April 3, 1963, for Metal-Free Lubricant Additives. The alkyl succinic anhydride discussed in this reference was prepared from a chlorinated polyisobutylene and maleic anhydride. The compounds of similar character discussed in the remainder of this disclosure were prepared by thermal condensation of non-chlorinated polyisobutylene and maleic anhydride. Either a chlorinated or a non-chlorinated polyisobutylene may be used to prepare additives for the purposes of the present invention. The alkyl or alkenyl radicals (mono or poly unsaturated) substituted in the succinic acid or succinic anhydride are commonly obtained from polyolefins such as polyethylene, polypropylene, polybutylene or copolymers of styrene or any other alkenyl group 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

copolymer resulting is predominately aliphatic in nature.

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.

It has been noted that at least ½ of a chemical equivalent of the amine per equivalent of substituted succinic acid or succinic anhydride should be used in the synthesis to produce a satisfactory product with respect to filming properties, and it is preferable to use one equivalent of polyamine per equivalent of succinic compound. It is not desirable to use more than two equivalents of polyamine per equivalent of succinic compound.

The reaction is believed to involve spontaneous salt formation and half amide formation upon heating to temperatures between 80 and 120° C. The third step is better carried out by reacting in xylene and removing the water by azeotropic distillation from 150 to 180° C.

Specific examples of the preparation of compounds for use according to the invention are set forth below:

EXAMPLE 1

A polyisobutenyl succinic anhydride was prepared by the reaction of polyisobutene with maleic anhydride at 250° C. The polyisobutenyl radical had an average molecular weight of 889 and the resulting alkenyl succinic anhydride was found to have an acid number of 94, corresponding to an equivalent weight of 596. To a mixture of 40 grams (0.067 equivalent) of this isobutenyl succinic anhydride and 15 mls. of xylene, there was added at room temperature 3.1 grams of diethylene triamine. The addition was made slowly and an initial exothermic reaction caused the temperature to rise to 60° C. The mixture was then 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. at atmospheric pressure. The residue was diluted with 50% xylene and used as an additive as referred to below.

EXAMPLE 2

The procedure of Example 1 was repeated using a polyisobutylene having an average molecular weight of 590. 28.3 grams of the polyisobutylene succinic anhydride were reacted with 3.4 grams of diethylene triamine, or in the proportions of ½ mol of polyamine to 1 mol of succinic compound.

EXAMPLE 3

The procedure of Example 1 was repeated using a polyisobutylene having an average molecular weight of 682. 20 grams of the polyisobutylene succinic anhydride were reacted with 2.0 grams of diethylene triamine, reacting in the proportions of ½ mol of polyamine to 1 mol of succinic compound.

EXAMPLE 4

The procedure of Example 3 was repeated using 1.33 grams of ethylene diamine.

EXAMPLE 5

The procedure of Example 3 was repeated using 1.08 grams of a commercially available polyamine mixture having the following composition by weight:

	Percent
Pentaethylene hexamine	33–35
Diethylene triamine	24–28
Triethylene tetramine	Trace
Higher polyethylene amines and substituted piperazines, etc.	Balance

EXAMPLE 6

The procedure of Example 3 was repeated using 1.33 grams of 1,3-diaminopropane.

EXAMPLE 7

The procedure of Example 3 was repeated using 2.8 grams of triethylene tetramine.

EXAMPLE 8

The procedure of Example 3 was repeated using 2.1 grams of 1,6-diaminohexane.

EXAMPLE 9

The procedure of Example 1 was repeated using 6.2 grams of diethylene triamine.

As controls, the following compounds were prepared using amines other than those forming the subject matter of the present invention:

EXAMPLE 10

The procedure of Example 3 was repeated, using 40 grams of polyisobutylene succinic anhydride and 7.25 grams of dimethylamino propylamine.

EXAMPLE 11

The procedure of Example 3 was repeated, using 3.4 grams of 1,8-diamino para-menthane.

It will be evident that other suitable polyamines may be used aside from those included in the examples. Among such compounds are tetraethylene pentamine, pentaethylene hexamine, decamethylene diamine, dipropylene triamine and homologues thereof.

Table I

Example	Amine	Mol Ratio of Polyamine to Polyisobutylene Succinic Anhydride	Molecular Weight of Polyisobutene
1	Diethylene triamine	0.5:1	889
2	do	9.5:1	590
3	do	0.5:1	682
4	Ethylene diamine	0.5:1	682
5	Polyamine H Special (a mixture of diethylene triamine, pentaethylene hexamine, etc.).	0.5:1	682
6	1,3-diamino propane	0.5:1	682
7	Triethylene tetramine	0.5:1	682
8	1,6-diamino hexane	0.5:1	682
9	Diethylene triamine	1:1	889
10	N,N-dimethylamino propylamine.	1:1	682
11	1,8-diamino-p-menthane	1:1	682

Table 1 summarizes certain information about the compounds produced in Examples 1 through 11. These materials 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 upon 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 in heat transfer which is desired. It is, therefore, impossible to state rigid rules for the quantity of additive which will apply in every case. However, the quantity of additive required is very small. For many purposes, additive feed of the order of 0.5 pint per 1,000 barrels to 1 pint per 1,000 barrels is sufficient. In general it can be stated that quantities greater than 17 gallons per 1,000 barrels will seldom be 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.

The addition to a petroleum charge stock of one of the products of the invention inhibits reduction in heat trans-

fer coefficient between the oil and the conductor in refinery processes, where the charge stock is thermally treated in passing through the conductor. 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 present invention remains preferentially with the liquid phase of the charge stock during the various refining stages. 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 residual and non-converted 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:

$$Q=UA\Delta t$$

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 sq. ft. 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 most cases, the percent heat transfer protection based on heat transfer coefficients is proportional to the percent inhibition of fouling based on the weight of fouling product formed.

The products listed in Table 1 were evaluated for effectiveness in improving heat transfer by the method previously described. The results of these tests are reported in Table 2. Each of the compounds listed in Table 1 was tested separately at a concentration of 150 p.p.m. based on volume in the charge stock, which was virgin light furnace oil, for 20 hours at temperatures ranging between 200° F. and 600° F., the procedure in each case was to heat up to about 600° F. in a time of about three hours and then hold at this higher temperature for the remainder of the test. In all cases the results obtained in the evalution of each additive were compared with control runs made prior to the testing of the material.

Table 2

Example (corresponds to Table 1)	Amine Derivative (where applicable)	Percent Fouling Inhibition	Percent Heat Transfer Protection
1	Diethylene triamine	84.2	77.8
2	do	84.1	53.1
3	do	76.8	82.4
4	Ethylene diamine	72.9	78.5
5	Polyamine H Special (a mixture of diethylene triamine, pentaethylene hexamine, etc.).	78.7	78.2
6	1,3 diamino propane	68.8	93.2
7	Triethylene tetramine	57.4	61.7
8	1,6 diamino hexane	54.4	27.9
9	Diethylene triamine	38.0	54.7
10	N,N-dimethylamino propylamine.	14.6	10.0
11	1,8 diamino-p-menthane	59.0	31.8
12	Ethoxylated N-akyl trimethylene diamine.	69.6	20.1
13	Alkyl-benzene sulfonic acid salt of a branched chain amine.	53.9	47.2

Table 2 shows test results and comparison with other materials which might be employed for similar purposes and are outside the invention. These data show positive benefit for materials within the scope of the invention.

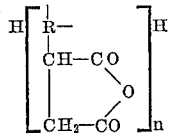
Examples 10 and 11 show comparative results for amine derivatives of succinic compounds using amines not within the scope of the invention, in these cases N,N-dimethylamino propylamine and 1,8-diamino-p-menthane. Example 12 shows that the results obtained with ethoxylated N-alkyl trimethylene diamine were not impressive. Example 13 shows that the results obtained from the amine salt of a petroleum sulfonic acid which has been used as an anti-foulant were comparable to the poorest results obtained with a compound of the present invention.

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.

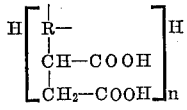
Having thus described my invention what I claim as new and desire to secure by Letters Patent is:

1. A process for preventing heat transfer reduction in a metal conductor, through which passes a hydrocarbon at a temperature between 200 and 1100° F., which comprises adding to said hydrocarbon 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:

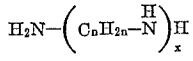


and alkyl-substituted and alkenyl-substituted succinic acids having the formula:



where 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 hydrocarbon chain; and

(b) a polyamine of the formula:



where n is an interger between 2 and 10 inclusive, x is an integer between 1 and 10 inclusive and C_nH_{2n} is a straight chain hydrocarbon, the proportions of polyamine varying from ½ to 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 polyamine are reacted in equal proportions by weight.

5. A process of claim 1, in which the polyamine is diethylene triamine.

6. A process of claim 1, in which the polyamine is a mixture of diethylene triamine, pentaethylene hexamine, and higher homologues.

7. A process of claim 1, in which the polyamine is 1,3-diamino propane.

8. A process of claim 1, in which the polyamine is 1,6-diamino hexane.

9. A process of claim 1, in which the polyamine is triethylene tetramine.

10. A process of claim 1, in which the polyamine is ethylene diamine.

No references cited.

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