June 14, 1960 P. R. CARL ET AL 2,940,922

METHOD OF INCREASING THE ON-STREAM TIME OF HEAT TRANSFER UNITS

Filed Oct. 8, 1957 3 Sheets-Sheet 3

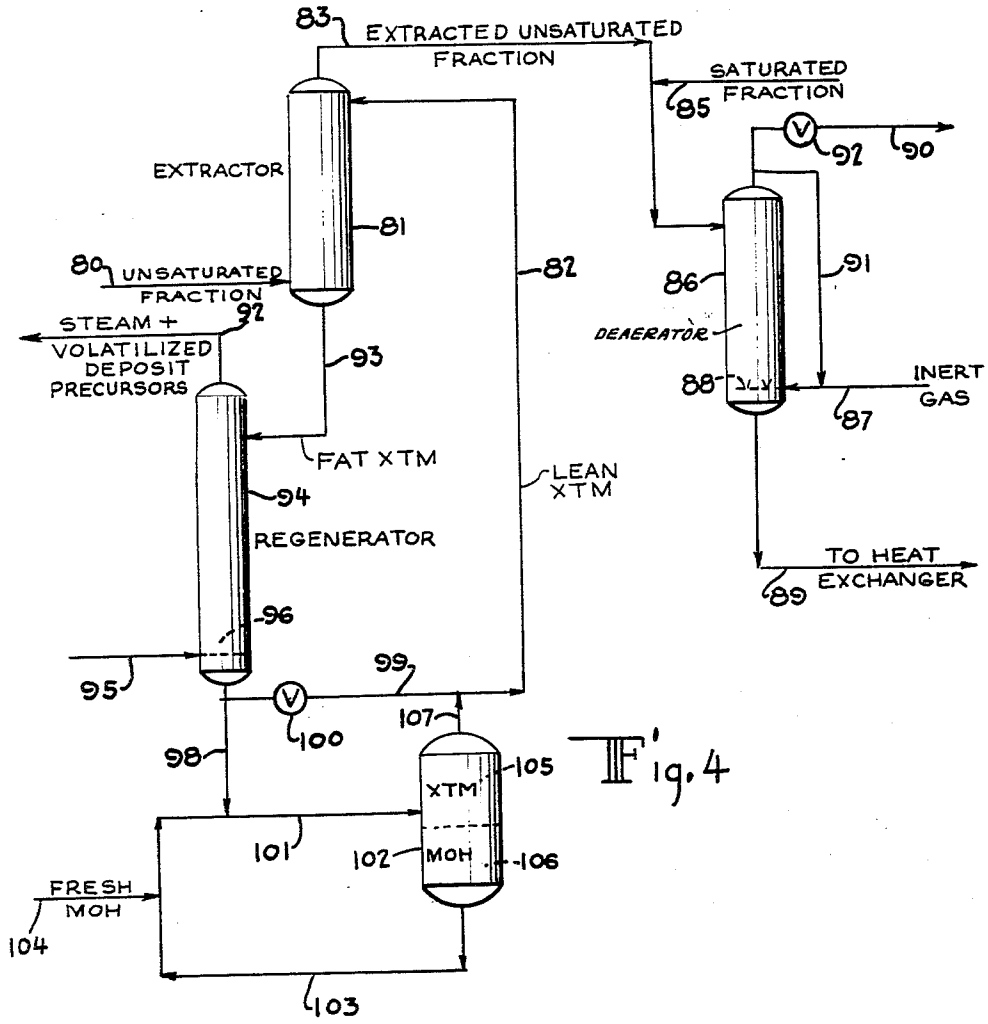



Fig. 4

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METHOD OF INCREASING THE ON-STREAM TIME OF HEAT TRANSFER UNITS

Filed Oct. 8, 1957 3 Sheets-Sheet 2

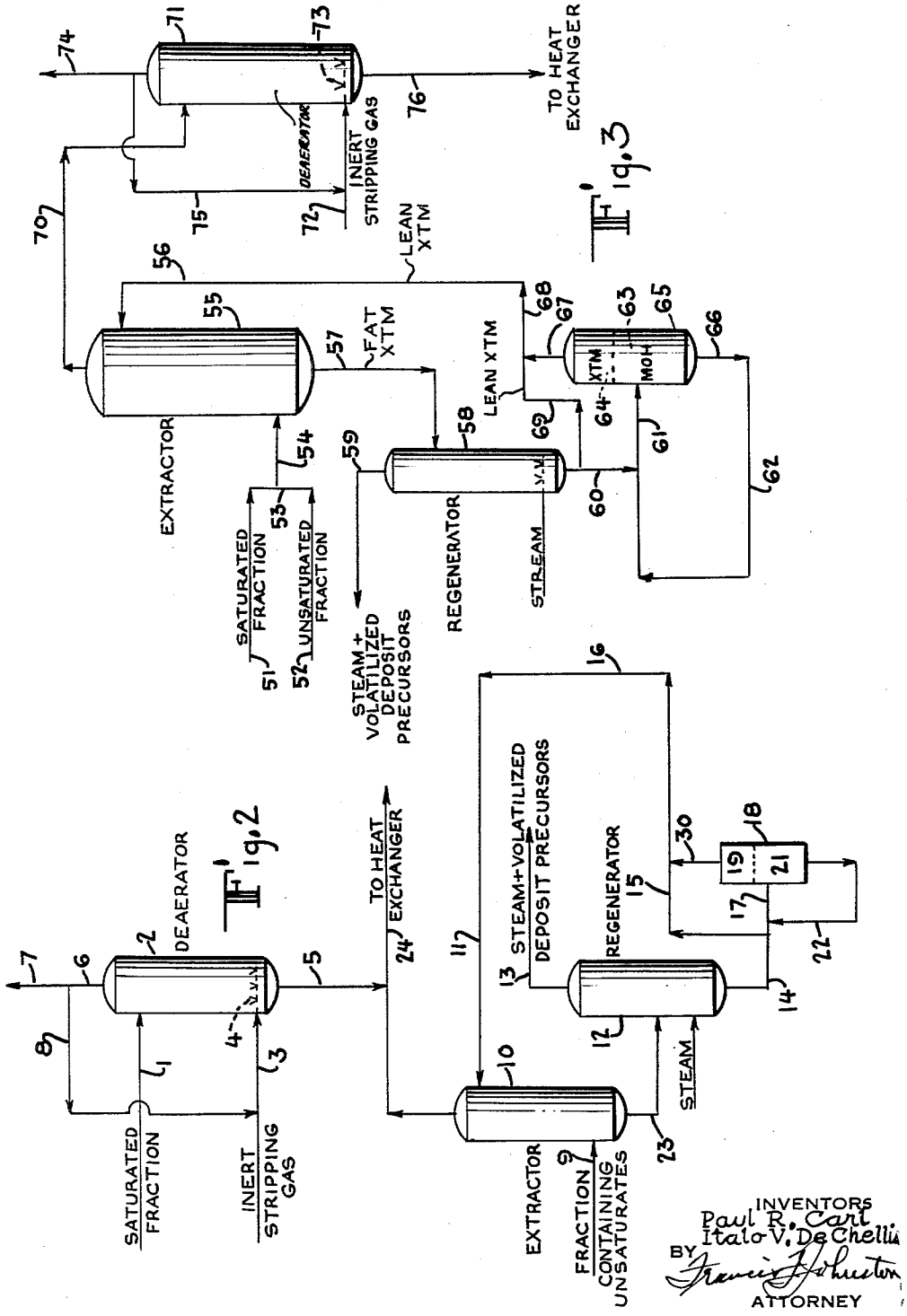



Fig. 3

Fig. 2

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METHOD OF INCREASING THE ON-STREAM TIME OF HEAT TRANSFER UNITS

Filed Oct. 8, 1957 3 Sheets-Sheet 3

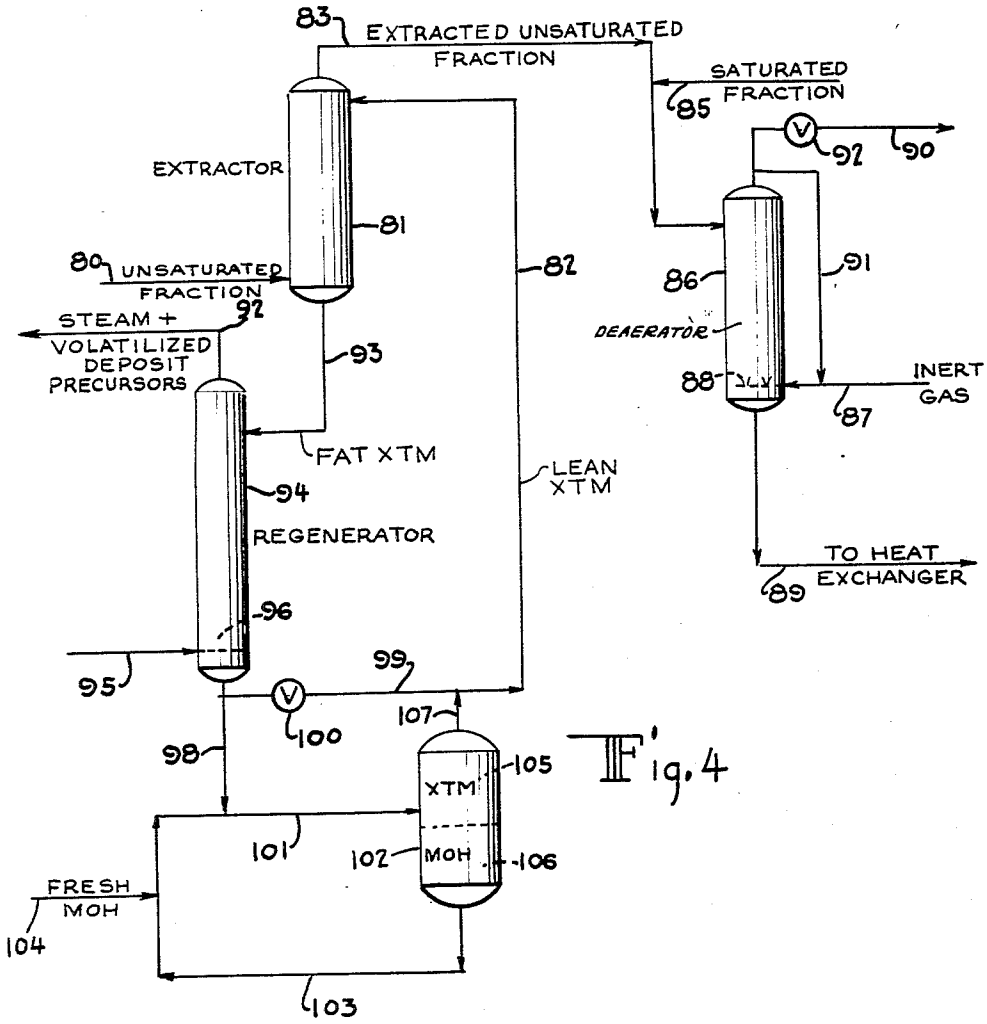



Fig. 4

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2,940,922

# METHOD OF INCREASING THE ON-STREAM TIME OF HEAT TRANSFER UNITS

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8 Claims. (Cl. 208—85)

The present invention relates to the precipitation of insulating deposits on heat transfer surfaces in contact with straight run or cracked petroleum fractions such as gasolines, naphthas, gas oils, heating oils, topped crudes and the like and, more particularly, to the treatment of straight run or cracked petroleum fractions such as gasolines, naphthas, gas oils, heating oils and the like prior to heating to temperatures of 350° F. and higher.

With the advent of reforming to produce gasolines of increased octane rating from naphthas and gasolines of lower octane rating than that required for modern high compression, spark ignited, internal combustion engines the problem of tube fouling in heat exchangers and furnaces has come to the fore. It has been found that petroleum fractions which deposit no sediment at ambient temperatures precipitate deposits of unknown composition on tube surfaces when heated to temperatures of 350° to 1200° F. in heat exchangers and furnaces. These deposits are of such magnitude that designed on-stream periods of, for example, 180 days are reduced to as little as 30 to 90 days.

For evaluating various methods of treating petroleum fractions of the class defined hereinbefore a tube-wall deposit testing method was developed. It has been established that the results so obtained are correlated with plant experience.

## TUBE-WALL DEPOSIT TEST

The instrument consists of an internally heated stainless steel tube having an inside diameter of ⅜ inch, an outside diameter of ½ inch and a length of 17⅝ inches. A selected amount of the petroleum fraction to be tested is passed at a pressure of 150 p.s.i.g. over the internally heated tube at a selected flow rate such that the petroleum fraction is heated to 500° F. during passage over the internally heated tube. The tube is weighed before and after contact with the selected amount of petroleum fraction being tested. The difference between the weight before and after is a measure of the on-stream time which heat transfer surfaces in contact with the selected petroleum fraction can be expected to have.

The test is carried out under conditions such that the petroleum fraction being tested is heated to 500° F. during passage over the internally heated tube because during the course of a large number of tests it was observed that practically all of the deposits are laid down in the 350°–550° F. temperature range. It was also observed that pressure and flow rate have much smaller effects upon the amount of deposit laid down than temperature. Therefore, in standard evaluation these two (pressure and rate of flow) were held constant to facilitate better control and reproducibility of results.

It would appear that the precipitation of sediment on tube surfaces when heated to temperatures of 350° F. and higher as measured by the aforedescribed test is the result of several reactions. Apparently oxygen dissolved in the oil promotes several polymerization type reactions that would not take place had the oil been oxygen free. Thus,



less sediment is deposited under the aforedescribed conditions from a fresh naphtha, i.e., one which has not been in storage or has been stored under a protective blanket of inert gas, than is precipitated from an aged naphtha, i.e., one which has been in storage a week or more in contact with the air. Deaeration is quite effective for increasing the thermal stability of various straight run and cracked naphthas.

The effect of aging and the effect of deaeration is manifest from the data presented in Table I.

*Table I*

Sedimentation test conditions:
Temperature ° F.—500; pressure, p.s.i.g.—150.
Naphtha flow rate, lbs./hr.—4; time, hours—5.
Deaeration conditions:
100 s.c.f. inert gas/barrel of naphtha.
Inert gas: Nitrogen.

| No. | Naphtha Type | Fouling Deposits, Mgms./20 lbs. | | Percent Reduction of Deposit |
|---|---|---|---|---|
| | | Before Deaeration | After Deaeration | |
| 1 | California Coker Fresh | 117 | 51 | 56 |
| 2 | California Coker Aged | 218 | 142 | 35 |
| 3 | {60% St. R. California / 40% California Coker (Fresh)} | 68 | 14 | 79 |
| 4 | {60% St. R. California / 40% California Coker (Aged)} | 167 | 103 | 38 |
| 5 | Mid-Cont. Coker (Fresh) | 26 | 11 | 58 |
| 6 | Calif. St. R. (Fresh) | 26 | 7 | 73 |
| 7 | Kuwait St. R. (Aged) | 45 | 4 | 91 |

It will be noted upon comparing the amount deposited before deaeration from fresh and aged California coker gasoline (items 1 and 2, Table I) that the deposit laid down by the aged coker naphtha is 86 percent greater than the deposit laid down by the fresh coker naphtha. Similarly, by comparing the amount of deposit produced as recorded in item 3 of Table I with that recorded in item 4 of Table I it will be found that the amount of deposit laid down by the blend of aged coker naphtha is 145 percent greater than that precipitated from the blend of fresh coker naphtha. It will also be noted that, while deaeration of the aged naphtha reduces the amount of sediment deposited by about 35 to 40 percent, deaeration of the fresh coker naphtha reduces the deposit about 56 percent.

The removal of dissolved oxygen by stripping with an inert gas such as nitrogen, hydrogen, $C_1$ to $C_4$ hydrocarbons or mixtures thereof is quite effective especially when the oil contains unsaturates. This is evidenced by the data presented in Table II.

*Table II*

Stripping conditions: 100 s.c.f. inert gas/barrel of naphtha (Inert gas—nitrogen).
Sedimentation test conditions:
Temperature, ° F.—500; pressure, p.s.i.g.—150.
Naphtha flow rate, lbs./hr.—4; time, hours—5.

| | Dissolved $O_2$, p.p.m. | Deposit, mgm./20 lbs. | Percent Reduction of Deposit |
|---|---|---|---|
| Naphtha Type: | | | |
| Calif. S.R.+5% Unsaturates | 27.0 | 316 | ---------- |
| Calif. S.R.+5% Unsaturates Deaerated | 0.2 | 118 | 63 |

However, deaeration alone is not effective to produce a fraction which will not decrease on-stream time when even fresh stock containing unsaturates is to be heated to temperatures of 350° to 1200° F. Thus, for example, a California coker gasoline without any treatment deposits 218 milligrams of material per 20 pounds of gasoline under the test conditions described hereinbefore,

When the coker gasoline was deaerated by blowing nitrogen therethrough the deposits were reduced to 142 milligrams per 20 pounds of gasoline. This represents an increased on-stream time of 50 percent which is still insufficient for practical purposes. However, when the coker gasoline is extracted with an aqueous alkaline solution of an alkali metal salt of at least one organic acid which solution is substantially mutually immiscible with an aqueous solution of alkali metal hydroxide the on-stream time is increased 170 percent.

*Table III*

STOCK TREATED—CALIFORNIA COKER GASOLINE

Deaeration conditions:
Inert gas—Nitrogen.
Temperature—50–100° F.
Amount of inert gas—100 s.c.f./b.
Extraction conditions:
Extraction medium—
19—KOH wt. percent.
50—KAP [1] wt. percent.
31—$H_2O$ Wt. percent
Temperature, ° F., 80–150° F.
Treating ratio: vols. oil/vol. extracting medium=10/1.
No. of stages—1.

| | Mgms. Deposit Per 20 Lbs. | Percent Reduction of Deposit | Increase In On-Stream Time, Percent |
|---|---|---|---|
| Untreated | 218 | | |
| Deaerated | 142 | 35 | 50 |
| Extracted and Deaerated | 82 | 62 | 170 |

[1] KAP—potassium salt of alkyl phenols boiling within the range of about 105° to about 650° F.

Accordingly, the present invention provides for increasing the on-stream time of heat exchangers in which petroleum fractions are in contact with metal surfaces at temperatures of about 350° to about 1200° F. by contacting the hydrocarbon fraction to be heated to temperature of about 350° F. or higher with an extracting medium comprising the organic salt phase of a liquid mixture comprising alkali metal hydroxide, alkali metal salt of at least one organic acid and water in proportions to form two mutually substantially immiscible liquid phases, one of said liquid phases being an aqueous organic salt phase containing the organic salt, alkali metal hydroxide and water, and the other liquid phase containing alkali metal hydroxide and water. Illustrative of the organic acids are phenols, especially alkyl phenols and particularly alkyl phenols boiling within the range of about 105° to about 650° F., saturated fatty acids having 4 to 12 carbon atoms in the molecule and particularly the branched fatty acids such as isobutyric acid. Of the alkali metals potassium is preferred. Since the extracting medium must be liquid at the extracting temperature, at temperatures below about 90° F. extracting mediums having a high concentration of isobutyrates must contain about 1 to about 5 percent of water-miscible aliphatic alcohols, ketones and the like such as alcohols, ketones and the like having 1 to 5 carbon atoms in the molecule. Typical of the preferred extracting medium are the potassium alkyl phenolate layer of liquid mixtures containing at least about 32 weight percent potassium hydroxide, about 1 to about 68 weight percent alkyl phenols and the balance water which separates into phenolate phase containing potassium alkyl phenolate, potassium hydroxide and water at a temperature of about 80° F. At lower extracting temperautres the potassium alkyl phenolate layer of liquid mixtures containing less alkyl phenols and potassium hydroxide can be used. When sodium salts of phenols are used it has been found that liquid mixtures containing at least 25 weight percent sodium hydroxide, about 1 to about 75 weight percent alkyl phenols and the balance water separate into a liquid aqueous organic salt layer and a substantially immiscible liquid aqueous sodium hydroxide layer at about 80° F. At lower extracting temperatures the sodium alkyl phenolate layer of liquid mixtures containing less alkyl phenols and sodium hydroxide can be used.

When a saturated hydrocarbon fraction, for example, straight run gasolines, is to be heated to 350° F. or above in admixture with an unsaturated fraction, e.g., cracked gasoline or coker gasoline, there are several combinations of treatments which lead to increased on-stream time. Thus, one can mix the saturated fraction and the unsaturated fraction in the proportion in which they appear in the mixture to be heated to 350° F. or higher and subject the mixture to extraction and deaeration. Various combinations of treatments are illustrated in the block diagrams presented in Figure 1. In studying Figure 1, it is to be observed that runs 8, 9 and 10 were made on the same material as that used in runs 2, 3, 4, 5 and 6 but after the mixture had aged for about one week.

The results graphically presented in Figure 1 are tabulated in Table IV.

*Table IV*

| Run No. | Mgms. Deposit Per 20 Lbs. of Mixture | Percent Reduction of Deposit | Increase in On-Stream Time, Percent |
|---|---|---|---|
| 1 | 60 | | |
| 2 | 32 | 47 | 90 |
| 3 | 18 | 70 | 230 |
| 4 | 32 | 47 | 90 |
| 5 | 32 | 47 | 90 |
| 6 | 4 | 93 | 1,300 |
| 7 | 72 | | |
| 8 | 4, 2 | 95, 97 | 2, 400 |
| 9 | 9, 8 | 88, 89 | 800 |
| 10 | 6 | 92 | 1, 150 |

It will be observed that extraction of the mixture of saturated hydrocarbon fraction and unsaturated hydrocarbon fraction, as exemplified by the mixture of straight run and coker gasoline in the proportion of 60:40 respectively, followed by deaeration and the extraction of the coker gasoline and deaeration of the mixture give substantially the same results (runs 6 and 10). These results are, within the limit of accuracy of the test, as good as those obtained by blowing the straight run with inert gas, extracting and deaerating the coker and deaerating the mixture (run 8). Therefore, the treatment represented by run 6 is preferred to that represented by run 8 because of the additional deaeration facilities required by the latter. However, the treatment represented by run 10 is preferred to that of run 6 or 8 because of the reduced amount of extracting medium required and the smaller facilities required for extracting 40 percent of the feed rather than the entire feed. However, when the coker flows directly from coking unit, and is free of dissolved oxygen, it is preferred to deaerate the straight run, extract the coker and mix the so-treated components of the mixture substantially immediately after treatment and substantially immediately before heating to about 350° F. or higher.

Illustrative of the preferred treatments given to a saturated hydrocarbon fraction and an unsaturated hydrocarbon fraction which are to be mixed and heated within the range of about 350° F. to about 1200° F., as exemplified by a mixture of 60 volumes of straight run gasoline (saturated hydrocarbon fraction) with 40 volumes of coker gasoline (unsaturated hydrocarbon mixture), are the treatments illustrated by the flow sheets Figures 2, 3 and 4.

Figure 2 provides for deaerating the saturated hydrocarbon mixture, extracting the unsaturated hydrocarbon mixture when the unsaturated fraction flows directly from the producing unit and contains substantially no dissolved oxygen, i.e., not more than 5 p.p.m. and mixing the treated mixtures substantially immediately after treatment and before heating within the range of about 380° F. to about 1200° F. At the present, it appears that treated stocks can be stored for a short period of time

and that while the preferred treatment is effective for aged stocks, nevertheless, it is preferred to treat the fractions as soon as produced.

In Figure 2 a saturated fraction such as straight run gasoline flows through line 1 to deaerator 2. The temperature maintained in deaerator 2 can be any temperature from ambient temperatures to sufficiently below the initial boiling point of the hydrocarbon fraction being treated that there is substantially no evaporation or distillation of the components of the fraction. Thus, a straight run gasoline having the following boiling range was deaerated at 80° F.

| Straight run gasoline: | ° F. |
|---|---|
| I.B.P. | 156 |
| 5% | 222 |
| 10% | 246 |
| 50% | 302 |
| 90% | 354 |
| E.B.P. | 392 |

An inert gas, for example, nitrogen, hydrogen, methane, ethane, propane, a mixture of hydrogen and light hydrocarbon such as reformer recycle gas substantially devoid of hydrogen sulfide and/or ammonia flows through line 3 to distributor 4 within deaerator 2. Distributor 4 is of any suitable design which provides distribution of the inert gas over the cross-section of deaerator 2 preferably as fine bubbles or streams of the inert gas. The deaerated saturated hydrocarbon fraction, in this instance straight run gasoline, flows from deaerator 2 through conduit 5. The inert gas together with oxygen from the saturated hydrocarbon fraction treated escapes from deaerator 2 through pipe 6. The inert gas can be vented through line 7 or recycled through line 8 until the oxygen content of the gas reaches saturation for the inert gas employed or until the oxygen content of the treated saturated hydrocarbon fraction is greater than about 0 to about 5 parts per million (p.p.m.).

The unsaturated hydrocarbon fraction to be treated containing substantially no dissolved oxygen flows through line 9 to extractor 10 which has at least one extraction stage and preferably a plurality, for example 2 or 3, of extraction stages. The extracting medium, e.g., the aforedescribed alkali metal alkyl phenolate phase flows through pipe 11 to extractor 9. The unsaturated hydrocarbon fraction, coker gasoline in this illustration, flows upwardly countercurrent to the downwardly flowing liquid aqueous extracting medium. In its passage countercurrent to the stream(s) of unsaturated hydrocarbon (coker gasoline) the extracting medium extracts the deposit or deposit precursors from the coker gasoline. The fouled or fat extracting medium leaves extractor 10 through line 23 through which it flows to regenerator 12. In regenerator 12 the fat extracting medium is steam distilled thereby volatilizing the deposit precursors which, together with excess steam are vented through line 13. The regenerated extracting medium flows from regenerator 12 through conduit 14 and pipes 15 and 16 back to pipe 11 and extractor 10 for treatment of further amounts of hydrocarbon fraction containing deposit precursors. Alternatively, a part or all of the regenerated extracting medium is diverted into pipe 17 where it is mixed with a substantially immiscible liquid aqueous alkali metal hydroxide solution. The mixture of regenerated extracting medium and liquid aqueous alkali metal hydroxide substantially immiscible with the regenerated extracting medium at a temperature within the range of about 60° F. to about 150° F. flows along pipe 17 to separator 18. In separator 18, at a temperature within the range of about 60° to about 150° F., the mixture separates into a regenerated extracting medium having the free alkali metal hydroxide content thereof fortified by migration of alkali metal hydroxide from the substantially immiscible liquid aqueous alkali metal hydroxide.

The regenerated, fortified extracting medium 19 flows through line 30 to pipe 15 and thence through pipe 16 to line 11 and extractor 10. The substantially immiscible liquid aqueous alkali metal hydroxide forms layer 21 and flows from separator 18 through pipe 22 back to pipe 17.

From extractor 10 the treated unsaturated hydrocarbon fraction (coker gasoline) flows through conduit 23 to line 24 where it is mixed with the deaerated straight run gasoline flowing from deaerator 2 through line 5. The mixture flows along pipe 24 to the heater, furnace, heat exchanger in which the mixture is to be heated to a temperature within the range of about 350° to about 1200° F.

The flow sheet Figure 3 illustrates in a highly diagrammatic manner the extraction of a mixture of a saturated hydrocarbon mixture such as straight run gasoline and of an unsaturated hydrocarbon mixture such as coker gasoline followed by deaeration of the so-treated mixture. This is illustrative of the treatment run 6 of Figure 1.

A saturated hydrocarbon fraction, e.g., straight run gasoline and an unsaturated hydrocarbon fraction such as coker gasoline which are to be heated together to a temperature within the range of about 350° to about 1200° F. prior to further treatment such as reforming, flow through pipes 51 and 52 respectively to pipe 53 where the two fractions mix and flow along pipe 54 to extractor 55.

Extracting medium comprising the liquid alkali metal organic salt layer of a liquid aqueous mixture comprising alkali metal hydroxide, organic acid and water in proportions to form a liquid, alkali metal organic salt layer contain free alkali metal hydroxide, alkali metal salt of an organic acid and water, and a liquid aqueous alkali metal hydroxide layer at a temperature within the range of about 60° to about 150° F. flows through conduit 56 to extractor 55.

The mixture of hydrocarbon fractions flows upwardly from pipe 54 through extractor 55 while the aforesaid extracting medium flows downwardly through extractor 55 from line 56. Through contact with the upwardly flowing hydrocarbon mixture the downwardly flowing extracting medium removes deposit precursors from the hydrocarbon mixture to produce a fat or fouled extracting medium which flows from extractor 55 through conduit 57. The fat extracting medium (fat XTM) flows into regenerator 58 where the fat extracting medium is steam distilled to volatilize the deposit precursors which, together with excess steam, are vented through pipe 59 while all or part of the regenerated extracting medium (lean XTM) flows from the regenerator 58 through pipe 60 to pipe 61. Liquid aqueous alkali metal hydroxide, substantially immiscible with lean extracting medium at a temperature within the range of about 60° F. and about 150° F. flowing through pipe 62, is mixed with the lean or regenerated extracting medium in pipe 61. The mixture flows through pipe 61 to separator 63 where at a temperature within the range of about 60° to about 150° F., a lean extracting medium fortified with respect to the concentration of free alkali metal hydroxide separates as an upper layer 64 from a substantially immiscible alkali metal hydroxide layer 65.

The alkali metal hydroxide layer is returned to pipe 61 through pipes 66 and 62. The fortified lean extracting medium flows from separator 63 through conduit 67 to pipe 68 and thence through pipe 56 by which it is recycled to extractor 55. All or part of the lean extracting medium can be diverted through conduit 69 to pipe 68 and thence recycled through pipe 56 to extractor 55.

Returning now to extractor 55, the treated mixture of hydrocarbons flows therefrom through conduit 70 to deaerator 71. An inert gas, e.g., nitrogen, hydrogen, methane, ethane, propane, or a mixture of hydrogen and hydrocarbons such as reformer recycle gas, flows from a source not shown through pipe 72 to distributor 73. The inert gas rises upwardly through the downwardly flowing extracted hydrocarbon mixture removing the oxygen therefrom. The inert gas with its load of oxygen

is vented from extractor 71 through pipe 74. When desired, the deaerating or stripping gas, together with its load of oxygen, can in part or wholly be recycled from pipe 74 through pipe 75 and pipe 72 to the deaerator. The oxygen content of the hydrocarbon mixture is reduced in stripper or deaerator 71 to not more than about 0 to about 5 p.p.m.

The stripped extracted hydrocarbon mixture flows from extractor 71 through conduit 76 to the furnace, heater, heat exchanger in which it is to be heated to a temperature within the range of about 350° to about 1200° F.

It will be noted that when the hydrocarbon mixture contains 40 volume percent unsaturated hydrocarbon fraction, the extractor for use in the treatment illustrated in Figure 3 must have about 2.5 times the capacity of the extractor used in the treatment illustrated in Figure 2. Similarly, the stripper used in the treatment illustrated in Figure 3 must have about 1.67 times the capacity of the stripper or deaerator used in the treatment illustrated in Figure 2. Consequently, for economic reasons, it is preferred to employ the treatment illustrated in Figure 2.

When the unsaturated hydrocarbon fraction contains dissolved oxygen, i.e., more than 5 p.p.m., it is preferred to pretreat the hydrocarbon fractions which are to be heated to 350° F. or higher in the manner illustrated in Figure 4.

Thus, the unsaturated hydrocarbon fraction containing dissolved oxygen flows through line 80 to extractor 81. In extractor 81 the unsaturated hydrocarbon fraction containing dissolved oxygen flows upwardly countercurrent to downwardly flowing lean extracting medium.

The extracting medium comprises the liquid alkali metal organic salt phase of a liquid mixture containing alkali metal orgaic salt, alkali metal hydroxide and water in proportions to form two substantially immiscible phases at temperatures of about 60° to about 150° F. One of said phases is the liquid alkali metal organic salt phase comprising alkali metal organic salt, alkali metal hydroxide, and water and the second phase comprises alkali metal hydroxide and water. The presently preferred extracting medium is the liquid alkali metal alkyl phenolate phase of a liquid mixture comprising alkali metal hydroxide, alkyl phenols boiling within the range of about 105° and about 650° F., and water in proportions to form two substantially immiscible phases at temperatures of about 60° to about 150° F., one of said phases being the aforesaid liquid alkali metal alkyl phenolate phase comprising alkali metal hydroxide, preferably potassium hydroxide, alkali metal alkyl phenolate and water and the other phase being the alkali metal hydroxide phase comprising alkali metal hydroxide, preferably potassium hydroxide, and water.

The lean extracting medium, i.e., lean liquid alkali metal organic salt phase, flows to extractor 81 through line 82. The extracted unsaturated hydrocarbon fraction flows from extractor 81 through conduit 83 to conduit 84 where it is mixed with untreated saturated hydrocarbon fraction flowing from a source not shown through line 85.

The mixture of extracted unsaturated hydrocarbon fraction and untreated saturated hydrocarbon fraction flows through conduit 84 to deaerator 86.

The mixture of extracted unsaturated hydrocarbon fraction and untreated saturated hydrocarbon fraction flows downwardly through deaerator 86 countercurrent to a stream of inert gas flowing into deaerator 86 through line 87 and distributor 88. The deaerator 86 is maintained at ambient temperature to a temperature below the boiling point of the fractions being deaerated. The deaerated mixture of extracted unsaturated hydrocarbon fraction and saturated hydrocarbon fraction flows from deaerator 86 through conduit 89 to the heat exchange system and further processing such as hydrocarbon conversion at temperatures of 350° F. or higher.

The inert gas and oxygen extracted from the mixture of extracted unsaturated hydrocarbon fraction and untreated saturated hydrocarbon fraction flows from deaerator 86 through line 90. All or a part of the inert gas flowing through line 90 can be recycled through line 91 by the control provided by valve 92 until the oxygen content of the mixture of hydrocarbons flowing from deaerator 86 through conduit 89 is greater than about 0 to 5 p.p.m.

Returning now to extractor 81, the extracting medium in flowing downwardly through extractor 81 in intimate contact with the unsaturated hydrocarbon fraction flowing upwardly through extractor 81 extracts deposit precursors from the unsaturated hydrocarbon fraction and is then termed "fat" extracting medium. The "fat" extracting medium flows from extractor 81 through line 93 to regenerator 94. In regenerator 94 the fat extracting medium flows downwardly countercurrent to steam introduced into regenerator 94 through line 95 and distributor 96. The steam volatilizes the deposit precursors in the fat extracting medium. The volatilized deposit precursors together with excess steam flow from regenerator 94 through pipe 97.

The regenerated extracting medium from which at least a major portion of the extracted deposit precursors have been volatilized is now termed "lean" extracting medium. The "lean" extracting medium flows from regenerator 94 through line 98. When the free alkali metal hydroxide content of the "lean" extracting medium is substantially that of the original extracting medium the regenerated extracting medium in part or wholly can be recycled to the extractor 81 through pipes 99 and 82 under control of valve 100. Alternatively, when the free alkali metal hydroxide content of the lean extracting medium has been reduced appreciably below that of the original extracting medium or at all times a part or all of the regenerated extracting medium flows through line 98 to pipe 101.

An aqueous solution of alkali metal hydroxide substantially immiscible with the regenerated extracting medium is circulated through pipe 101, settler 102 and pipe 103, fresh alkali metal hydroxide being introduced as necessary through pipe 104 from a source not shown.

The lean extracting medium flows from pipe 98 into pipe 101 and mixes therein with the substantially immiscible aqueous alkali metal hydroxide. The mixture flows to settler 102 where the regenerated extracting medium fortified with respect to the free alkali metal hydroxide content thereof through migration of alkali metal hydroxide from the fortifying immiscible aqueous alkali metal hydroxide separates from the immiscible aqueous alkali metal hydroxide to form phase or layer 105. The mixture of regenerated or "lean" extracting medium and fortifying immiscible aqueous alkali metal hydroxide is maintained at a temperature within the range of about 60° to about 150° F. until the lean fortified extracting medium 105 separates from the immiscible fortifying aqueous alkali metal hydroxide phase 106.

The fortified "lean" extracting medium flows from settler 102 through line 107 to conduit 99 and thence through line 82 to extractor 81.

Thus, it is apparent to those skilled in the art that the present invention provides a means for treating an unsaturated hydrocarbon fraction or a saturated hydrocarbon fraction or a mixture of unsaturated hydrocarbon fraction and saturated hydrocarbon fraction which is to be heated to 350° F. or higher to increase the on-stream time of heat exchange units which means comprises extracting at least the unsaturated hydrocarbon fraction with a liquid extracting medium comprising the liquid alkali metal organic salt phase of a liquid mixture comprising alkali metal hydroxide, organic salt as hereinbefore defined and water in proportions to form two substantially immiscible phases or layers at a temperature within the range about 60° to about 150° F., said two substantially immiscible phases or layers being (1) a liquid alkali metal organic salt layer comprising alkali metal hydroxide, alkali metal organic salt and water and (2) a liquid alkali metal hydroxide layer or phase comprising alkali

metal hydroxide and water. It is preferred that the organic salt be the alkali metal hydroxide salt of alkyl phenols boiling within the range of about 105° and about 650° F. and that the alkali metal hydroxide be potassium hydroxide.

We claim:

1. A method of increasing the on-stream time of heat exchanger surfaces operating at elevated temperatures of at least 350° F. in contact with a mixture of straight run and cracked petroleum fractions boiling above 100° F. which comprises, prior to subjecting said mixture to said elevated temperature environment, contacting at least the cracked fraction with a liquid extracting medium comprising the liquid aqueous salt phase of a mixture containing organic acid, alkali metal hydroxide and water in proportions to form at a temperature within the range of about 60° F. to about 150° F. a salt phase comprising alkali metal hydroxide, alkali metal salt of said organic acid and water, and a substantially immiscible liquid alkali metal hydroxide phase comprising aqueous alkali metal hydroxide, separating treated hydrocarbon fraction from fouled extracting medium, passing an inert gas through at least the straight run fraction to deaerate said fraction and to reduce the oxygen content thereof to not more than 5 p.p.m., mixing said deaerated fraction with said treated fraction, and thereafter heating said mixture to a temperature of at least 350° F.

2. A method of increasing the on-stream time of heat exchanger surfaces operating at elevated temperatures of at least 350° F. in contact with a mixture of straight run and cracked petroleum fractions boiling above 100° F. which comprises, prior to subjecting said mixture to said elevated temperature environment, contacting a cracked petroleum fraction boiling within the range of 100° F. and 900° F. with a liquid extracting medium comprising the phenolate salt phase of a liquid mixture comprising alkali metal hydroxide, alkyl phenols and water in proportions to form at a temperature within the range of about 60° F. and about 150° F. a phenolate salt phase comprising alkali metal hydroxide, alkali metal alkyl phenolate and water, and a substantially immiscible alkali metal hydroxide phase comprising alkali metal hydroxide and water, separating treated cracked petroleum fraction from extracting medium, passing inert gas through a straight run petroleum fraction to deaerate said fraction and reduce the oxygen content thereof to not more than 5 p.p.m., mixing said treated cracked petroleum fraction and said deaerated straight run fraction, and thereafter heating said mixture to a temperature of at least 350° F.

3. A method of increasing the on-stream time of heat exchanger surfaces operating at elevated temperatures within the range of about 350° to about 1200° F. in contact with a mixture of straight run and cracked petroleum fractions boiling above 100° F. which comprises, prior to subjecting said mixture to said elevated temperature environment, mixing a straight run petroleum fraction and a cracked petroleum fraction to form a feed mixture contacting said feed mixture with an extracting medium comprising the organic salt phase of a liquid mixture comprising alkali metal hydroxide, alkyl phenols and water in proportions to form at a temperature within the range of about 60° and about 150° F. two substantially immiscible liquid phases, one of said phases being an organic salt phase comprising alkali metal hydroxide, alkali metal alkyl phenolate and water, and the other of said phases comprising aqueous alkali metal hydroxide solution, separating treated feed mixture from fouled extracting medium, passing an inert gas through said treated feed mixture to reduce the oxygen content of said feed mixture to 0 to 5 p.p.m. to produce a deaerated treated feed mixture, and heating said deaerated treated feed mixture to a temperature within the range of about 350° to about 1200° F.

4. A method of treating reformer charge stock to increase the on-stream time of heat transfer surfaces operating at elevated temperatures within the range of about 350° to about 1200° F. which comprises, prior to subjecting said reformer charge stock to said elevated temperature environment, contacting a cracked gasoline with an extracting medium comprising the liquid alkali metal alkyl phenolate phase of a liquid mixture comprising alkali metal hydroxide, alkyl phenols, and water in proportions to form two substantially immiscible liquid phases at a temperature within the range of about 60° and about 150° F., one of said liquid phases being an alkali metal alkyl phenolate phase comprising alkali metal hydroxide, alkali metal alkyl phenolate and water, and the other of said liquid phases being an alkali metal hydroxide phase comprising alkali metal hydroxide and water, separating treated cracked gasoline from fouled extracting medium, passing an inert gas through a straight run gasoline to reduce the oxygen content thereof to 0 to 5 p.p.m. and to obtain a deaerated straight run gasoline, mixing said treated cracked gasoline and said deaerated straight run gasoline to form a reformer feed stock thereafter heating said reformer feed stock to reforming conditions including elevated temperatures of at least 350° F. and recovering reformed feed stock.

5. The method of treating reformer charge stock to increase the on-stream time of heat transfer surfaces operating at elevated temperatures within the range of about 350° to about 1200° F. as set forth and described in claim 4 wherein the alkyl phenols boil within the range of about 105° and about 650° F., and the alkali metal hydroxide is potassium hydroxide.

6. The method of treating reformer charge stock to increase the on-stream time of heat transfer surfaces operating at elevated temperatures within the range of about 350° to about 1200° F. as set forth and described in claim 4 wherein the alkyl phenols boil within the range of about 105° and about 650° F., wherein the alkali metal hydroxide is potassium hydroxide, wherein the reformer feed stock is reformed in the presence of solid, particle-form reforming catalyst and hydrogen-containing recycle gas, and wherein the deaerating inert gas is the aforesaid hydrogen-containing recycle gas.

7. A method of treating a hydrocarbon conversion charge stock comprising a saturated hydrocarbon fraction and a fraction containing unsaturated hydrocarbons, both fractions boiling above 100° F. and below about 900° F., to increase the on-stream time of heat transfer surfaces operating at elevated temperatures within the range of about 350° to about 1200° F. in contact with said hydrocarbon conversion charge stock which comprises, prior to subjecting said hydrocarbon conversion charge stock to said elevated temperature environment, contacting a fraction containing unsaturated hydrocarbons boiling above about 100° F. and below about 900° F. with an extracting medium comprising the liquid alkali metal alkyl phenolate phase of a liquid mixture comprising alkali metal hydroxide, alkyl phenols, and water in proportions to form at a temperature within the range of about 60° and about 150° F. two substantially immiscible liquid phases, one of said liquid phases being a liquid alkali metal alkyl phenolate phase comprising alkali metal hydroxide, alkali metal alkyl phenolate and water, and the other liquid phase being an alkali metal hydroxide phase comprising alkali metal hydroxide and water, separating treated fraction containing unsaturated hydrocarbons from fouled extracting medium, passing an inert deaerating gas through said saturated hydrocarbon fraction to reduce the oxygen content thereof to about 0 to about 5 p.p.m. to obtain a deaerated saturated hydrocarbon fraction, mixing said treated fraction containing unsaturated hydrocarbons with said deaerated saturated hydrocarbon fraction to obtain a hydrocarbon conversion charge stock, and thereafter heating said hydrocarbon conversion charge stock to a conversion temperature higher than about 350° F.

8. The method of treating a hydrocarbon conversion

charge stock comprising a saturated hydrocarbon fraction and a fraction containing unsaturated hydrocarbons as set forth and described in claim 7 wherein the alkyl phenols boil within the range of about 105° and about 650° F., wherein the alkali metal hydroxide is potassium hydroxide, and wherein the deaerating inert gas is hydrogen-containing gas.



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