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TREATING OF HEAVY OILS TO REMOVE METALS, SALTS AND COKE FORMING MATERIALS EMPLOYING A COMBINATION OF AN ALCOHOL, ORGANIC ACID AND AROMATIC HYDROCARBON

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Fig. 2

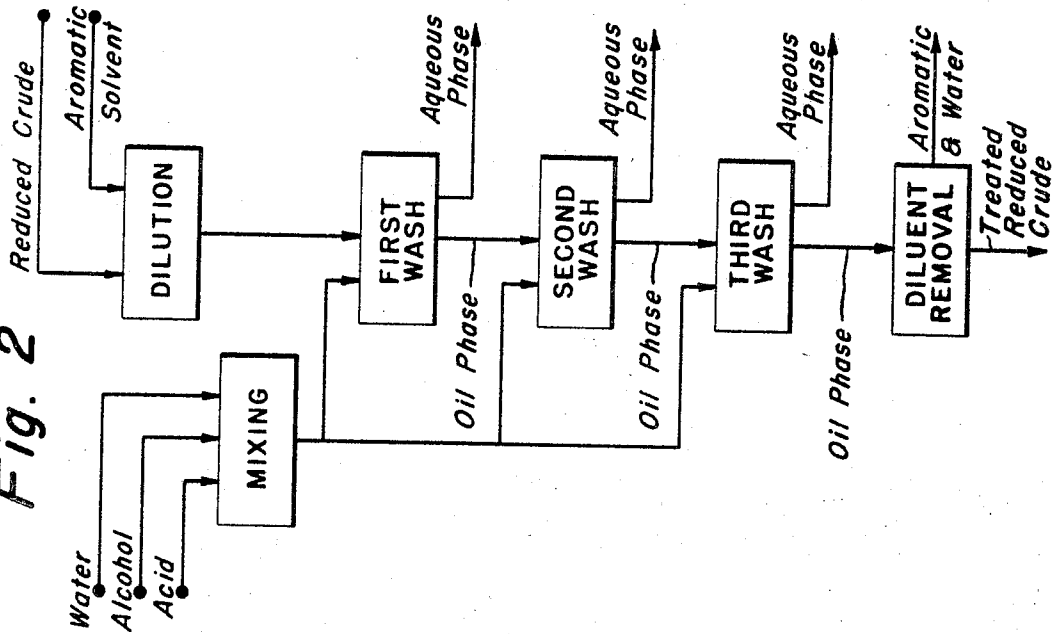
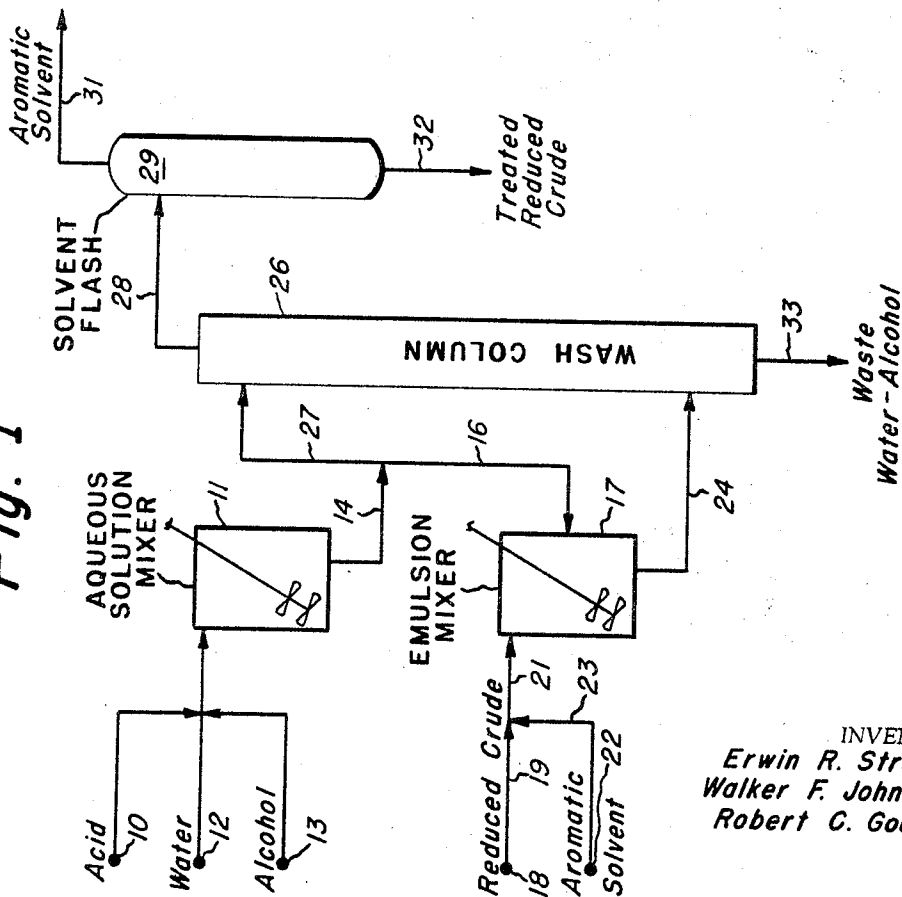


Fig. 1



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TREATING OF HEAVY OILS TO REMOVE METALS, SALTS AND COKE FORMING MATERIALS EMPLOYING A COMBINATION OF AN ALCOHOL, ORGANIC ACID AND AROMATIC HYDROCARBON

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ABSTRACT OF THE DISCLOSURE

A heavy oil is treated to remove therefrom metals, salts, and coke forming materials. The treating method comprises: dissolving a solvent comprising aromatic hydrocarbons having 6 to 9 carbon atoms per molecule in the oil; mixing therewith an aqueous liquid treating solution containing about 1 to about 30 volume percent of a water soluble alcohol and having a pH in the range of about 4 to about 9 to form a treated oil; separating the treating solution from the treated oil; and recovering the treated oil which contains substantially reduced amounts of metals, salts, and coke forming materials.

This invention relates to treating of heavy oils. More particularly, the invention concerns a method for removing deleterious materials such as, for example, metals and coke forming materials from heavy petroleum oils such as reduced crude.

The presence of metals in petroleum hydrocarbon fractions, particularly the heavier fractions boiling above about 700° F., have long been recognized as deleterious catalyst poisons during refining of these materials. The metals in these fractions, primarily nickel and vanadium, are deposited on the solid catalyst resulting in poisoning of desired catalytic activity and, in some cases, catalyzing undesirable side reactions. Refining processes in which the presence of such metals is particularly harmful are catalytic cracking and hydrocracking.

Some metal compounds are volatile and are distilled overhead with heavy oils during vacuum distillation of crude oil to produce feedstocks for refining into more valuable products such as gasoline and jet fuel. The metals problem has become particularly serious in modern refineries employing vacuum distillation at a pressure of 50 mm. mercury absolute and lower in order to recover a maximum amount of feedstock for catalytic cracking. The distillate from such vacuum distillation units contains many useful hydrocarbons having boiling points well above 1,000° F., however such distillate usually also contains harmful volatile metal compounds such as porphyrins.

Other deleterious materials often found in heavy oils include nitrogen compounds, carbonaceous residues and salts of various kinds. Processing of heavy oils is greatly enhanced and longer periods of trouble-free operation result from removal of deleterious materials from the heavy oil feed to processes utilizing such oils as feed. By the term heavy oils as used herein is meant hydrocarbon oils boiling above about 900° F. and materials containing significant amounts of such oils, even though the oils may be solid or semi-solid at normal atmospheric temperature. The term thus includes materials which may be distilled overhead as well as distillation bottoms such as reduced crude oil.

Accordingly, this invention provides a method for treat-

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ing heavy oils containing deleterious materials to remove such materials therefrom, which method comprises dissolving into said oil an aromatic solvent, mixing with said solvent-containing oil an aqueous liquid treating solution containing about 1 to about 30 volume percent of a water soluble alcohol, said treating solution having a pH in the range of about 4 to about 9, separating said solution from said oil and recovering treated oil containing a lesser amount of deleterious materials than untreated oil. It is preferable to use aromatic hydrocarbons having 6 to 9 carbon atoms per molecule such as benzene, toluene, the xylenes, ethylbenzene, cumene, etc. as the aromatic solvent. Benzene is a preferred solvent.

The treating solution comprises water and about 1 to 30% by volume of alcohol. Preferred treating solutions contain about 10 to 25 vol. percent isopropanol or about 1 to 10 vol. percent amyl alcohol, the percentage being based on the treating solution.

The pH of the treating solution should be in the range of about 4 to 9, suitably about 4-6 or about 7.5-8.5. Preferably the pH of the treating solution is adjusted to within the range of about 4 to 6 by addition thereto of a water soluble carboxylic acid. The acid preferably is one having 1 to 6 carbon atoms per molecule, acetic acid being a preferred acid.

FIGURE 1 is a schematic flow diagram of a continuous flow system for conducting the process of this invention.

FIGURE 2 is a schematic diagram illustrating the steps in conducting a preferred embodiment of a batch process for conducting the process of this invention.

Briefly, the process of the present invention embodies dilution of the heavy oil with aromatic hydrocarbon and thoroughly contacting this mixture with an alcohol-water treating solution which has preferably been acidified with addition of a carboxylic acid. After the thorough contacting, the aqueous phase and the oil phase are separated. The aqueous phase containing the deleterious materials from the oil is removed as a bottoms product for disposal. The upper oil layer is flashed, or stripped, to recover aromatic solvent for reuse and the cleaned treated oil is recovered. Either batch or continuous processing techniques or a combination of the two may be employed.

A preferred embodiment of a continuous process will now be described in conjunction with FIGURE 1. Acid, such as acetic acid, from source 10 is passed into aqueous solution mixer 11 along with water from source 12 and alcohol, preferably isopropanol, from source 13. The alcohol, water and acid are thoroughly mixed in the mixer 11 and withdrawn and passed via lines 14 and 16 into emulsion mixer 17. Heavy oil to be treated, for example reduced crude, from source 18 is passed via line 19 and line 21 into the emulsion mixer 17. Aromatic solvent, such as benzene, from source 22 is passed via line 23 into admixture with reduced crude from line 19 and the mixture passed via line 21 into the emulsion mixer 17. At least enough aromatic solvent is used so that the heavy oil-aromatic mixture has a specific gravity lower than that of the aqueous alcohol solution. The aqueous treating mixture and the reduced crude-solvent are thoroughly emulsified in the emulsion mixture 17. The emulsion is passed via line 24 into the wash column 26 wherein the oil and water phases are separated. Aqueous treating solution from the mixer 11 is passed via line 14 and line 27 into the upper portion of the wash column 26 wherein the aqueous phase descends countercurrently to the rising oil phase aiding in breaking the emulsion and effecting further treating. The column may be packed with any suitable packing such as Berl saddles, etc. to effect contact between the phases. Treated oil containing aromatic solvent is withdrawn from the wash column 26 through line 28 and passed into solvent flash drum 29 from which aromatic solvent is withdrawn overhead via

line 31 and treated reduced crude containing a lesser amount of deleterious material is withdrawn from the bottom via line 32. Waste water-alcohol solution is withdrawn from the wash column 26 via line 33.

Referring now to FIGURE 2, a preferred embodiment of a batchwise process for carrying out the present invention will be described. Reduced crude is thoroughly mixed with an equal volume of aromatic solvent, preferably benzene. The benzene-reduced crude mixture is then contacted in a batch tank with a solution containing 25 percent isopropanol in water with sufficient acetic acid to adjust the pH of the treating solution to about 5. Preferably, three separate washings with the treating solution are effected, with disposal of the aqueous phase following each wash. Equal volumes of treating solution and diluted oil are used during each of the three washings illustrated in FIGURE 2. In the batch process emulsion is not formed, although some form of mixing is preferably used during the washes. Normally, bubbling of natural gas through the diluted reduced crude-aqueous mixture provides sufficient mixing and the gentle agitation aids in separation of the oil and water phases. The water and oil phases separate rapidly and a stable emulsion is not formed during the use of the batchwise technique. The oil phase normally contains less than 5% water. The benzene and traces of water and alcohol are removed from the oil phase by flashing or stripping with gas to produce a treated reduced crude product.

EXAMPLE

Properties of raw and treated reduced crude product from batchwise treating as described above are shown in Table I.

TABLE I.—PROPERTIES OF RAW AND TREATED 6% REDUCED CRUDE

	Raw	Treated
Gravity, ° API.....	10.5	11.2
Distillation, ° F.:		
IBP.....	680	650
6 Vol. Percent at (° F.).....	1,000	1,000
Ramsbottom carbon, wt. percent.....	15.5	6.0
Ash, wt. percent.....	0.17	0.03
Sulfur, wt. percent.....	0.9	0.9
Nitrogen, p.p.m. (parts per million parts by weight):		
Total.....	5,600	2,900
Basic.....	2,000	1,500
Metals, p.p.m.:		
Na.....	400	5
Ni.....	30	17
V.....	27	26
Ca.....	31	25
Mg.....	12	4
Fe.....	65	25

About 99% of the sodium was removed from the reduced crude as sodium chloride. Some unexpected benefits arising from treating by the process of this invention include the reduction of Ramsbottom carbon from 15.5 to 6.0 wt. percent, and removal of about 50% of the nitrogen compounds. There also was a considerable reduction in the nickel, iron, magnesium and calcium contents of the reduced crude. All of these benefits were obtained with a negligible treating loss of less than 0.5 wt. percent of the reduced crude. The run length of a

catalytic process using solid catalyst pellets was several-fold longer when processing this treated heavy oil than when raw untreated oil was used as feed (at least 64 days as compared with 3-4 days).

While the invention has been described in conjunction with specific embodiments thereof, such should not be deemed to limit the scope of the invention. Other embodiments and alternatives will be apparent to those having skill in the art from the above description and such are to be deemed within the scope of the invention.

Having described the invention, what is claimed is:

1. A method for treating a heavy oil containing deleterious materials including metals, salts, and coke forming materials to remove said deleterious materials therefrom, which method comprises: dissolving into said heavy oil an aromatic solvent comprising aromatic hydrocarbons having 6 to 9 carbon atoms per molecule to form a solvent-containing oil; mixing with said solvent-containing oil an aqueous liquid treating solution to produce a treated oil, said treating solution containing about 1 to about 30 volume percent of a water soluble alcohol and having a pH in the range of about 4 to about 9; separating said treating solution from said treated oil; and recovering said treated oil containing an amount of deleterious materials that is substantially reduced from that of the untreated oil.

2. The method of claim 1 wherein said aromatic solvent comprises benzene.

3. The method of claim 1 wherein prior to said mixing the pH of said treating solution is adjusted to within the range of about 4 to 6 by addition thereto of a water soluble carboxylic acid.

4. The method of claim 3 wherein said acid is an aliphatic acid having 1 to 6 carbon atoms per molecule.

5. The method of claim 4 wherein said acid is acetic acid.

6. The method of claim 1 wherein said alcohol is isopropanol in an amount of between about 10 to about 25 percent by volume based on said solution.

7. The method of claim 1 wherein said alcohol is amyl alcohol in an amount of between about 1 and about 10 percent by volume based on said solution.

8. The method according to claim 1 wherein said solvent is dissolved in said oil in an amount of between about 25 and about 150 percent by volume based on said oil, said alcohol has in the range of 1 to 6 carbon atoms per molecule, and the pH of said treating solution is adjusted to within the range of about 4 to about 6 by addition to said solution of a monobasic carboxylic acid having 1 to 6 carbon atoms per molecule.

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