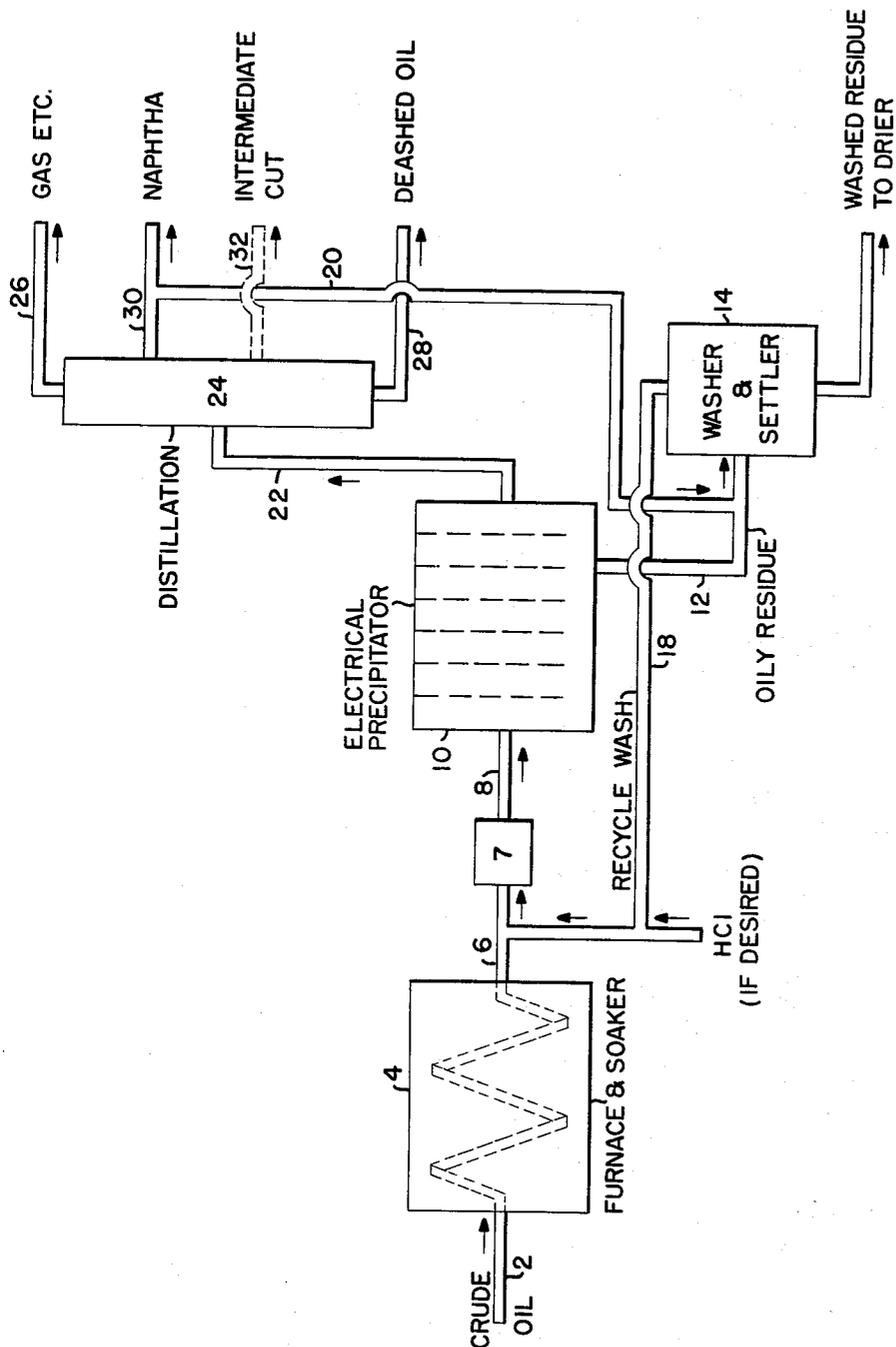


Aug. 15, 1961

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CONTAMINATED RESIDUAL PETROLEUM FRACTION
Filed June 25, 1958

2,996,442



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PROCESS FOR ELECTRICALLY TREATING A METALLIC CONTAMINATED RESIDUAL PETROLEUM FRACTION

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Filed June 25, 1958, Ser. No. 744,597
8 Claims. (Cl. 204-184)

The present invention relates to the removal of metallic contaminants from petroleum oils and more particularly relates to an improved process for the removal of complex organo-metallic compounds of the porphyrin type from high boiling petroleum gas oils and in particular from residual oils.

The use of residual hydrocarbon oils, either alone or mixed with, for example, oil distillates as fuel for gas turbines is highly economically attractive. However, the ash forming constituents generally occurring in residual hydrocarbon oils constitute a severe drawback to the use of the latter as fuel oil for this purpose. The ash forming constituents, which in all probability are non-volatile porphyrins associated in particular with vanadium, nickel and iron, have a severe fouling and corrosive effect upon installations in which the oils are used. They attack the refractories used to line boilers and combustion chambers, and corrode turbine blades.

Though numerous methods have been proposed for removing these contaminants from high boiling hydrocarbon oils, they have been largely ineffective, generally resulting in loss of substantial quantities of oil, and in most cases are prohibitively expensive. It has hitherto been suggested to coagulate the metal with a coagulant or a solvent, but separation and filtration are difficult, expensive, time consuming and inefficient.

It is a principal object of the present invention to provide an improved process for treating metal-contaminated heavy hydrocarbon oils, and in particular residual oils. A further object of the present invention is to provide a process wherein asphaltenes and porphyrins are more economically removed from hydrocarbon oils.

These objects will be more clearly understood and other objects will be evident from the detailed description of the invention.

Now, in accordance with the present invention, it has been found that these objects may be realized by a process wherein a heavier hydrocarbon oil which contains undesirable metallic impurities is initially subjected to an extended thermal treatment. Thereafter, the heat-soaked oil is passed to a mixing zone wherein it is diluted with a light hydrocarbon having at least 3 carbon atoms. A naphtha fraction boiling in the range of 55° to 400° F. is particularly suitable. The mixture may, if desired, be treated with an acidic gas soluble in the oil, such as HCl, SO₂, BF₃, and the like. The mixture is then subjected to an electrical field which effectively serves to coagulate the particles. It is surprising that the metal-containing particles resulting from high temperature (600° to 800° F.) heat soaking step are electrically charged. Though an alternating current is completely ineffective, if a direct current is used, the coagulation is rapid and the precipitate deposits on the cathode from which it is readily separated by vibration, current reversal, or other means.

The concentration of metallic constituents in crude oil varies from 1 to 500 parts per million and most of this is concentrated in the residual fraction. Heavy gas oils distilled from typical crudes may contain from 1 to 20 pounds of metallic contaminants per 1000 barrels, while residual fractions may contain as much as 200 pounds per 1000 barrels.

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Turning now to the drawing which shows a preferred embodiment of the present invention, a crude oil is passed via line 2 to thermal treating zone 4. This is preferably a combination furnace and soaker vessel, with temperatures and pressures maintained to provide no more than incipient cracking, so that no significant amount of lighter components are formed. The conditions required will depend upon a combination of time and temperature, the nature of the feed stock and the like. The temperatures of thermal treatment, however, are below about 900° F. and above about 600° F. to ensure sufficient reaction rate. Preferably, temperatures from 650° to 850° F. are applied. Pressures of 200 to 1500 p.s.i.g. may be applied to maintain the material in a substantially liquid state. A residence period of 0.1 to 10 hours, preferably 0.3 to 5 hours, is maintained.

The heat soaked feed is now passed via line 6 into mixing zone 7 where it is diluted, without the necessity of cooling it, with 0.1 to 10 volumes, preferably 0.3 to 3 volumes, of a light hydrocarbon, preferably a naphtha fraction boiling in the range of 55° to 300° F. Precipitation of a light, flocculent precipitate occurs, the addition of the diluent having reduced the temperature of the mixture to about 200° to 400° F. It is advantageous to add at this stage or subsequently, an acidic gas such as HCl, SO₂, BF₃, or other hydrogen halide. The amount of this auxiliary coagulating reagent employed may vary from 0.1 to 5% on feed.

The mixture of oil, solvent, and precipitate is passed through line 8 to electrical precipitation zone 10, which, though it may be of conventional design, is preferably a direct current precipitator and the mixture subjected to the effects of an electrical field. One or more cathodes are employed, preferably equipped with vibrating means to remove deposited material. The voltage between the electrodes may be varied appreciably and be in the range of from 1,000 to 50,000 volts. The temperature within the electrical precipitator 10 is in the range of about 200° to 400° F.

The coagulated residue is withdrawn as a semi-fluid or slurry and passed via line 12 to wash-settling vessel 14. Here the residue may be washed with fresh naphtha admitted through line 20 to remove occluded oil. The washed residue may be separated from the wash liquid by settling and the wash liquid recycled via line 18 to dilute the incoming heat-treated feed. It is understood that other means of separating occluded oil from the precipitated metal residue may be employed. Thus a second electrical precipitation step may be used, or the washing step may be carried out in a filter or other conventional means. The washed residue may be dried, as by spray drying, and employed as fuel or as desired. By operating in the manner described, the oil removed from the precipitate is returned to the process for ultimate recovery.

Returning now to precipitator 10, the oil layer is passed to distillation tower 24 via line 22 where the desired naphtha cut employed as solvent is taken overhead through line 30; light gases are withdrawn through line 26; and an intermediate cut may be withdrawn through line 32. Demetallized oil is taken as a bottoms cut through line 28, and is found to be substantially improved not only in metals content but also in such important respects as carbon-forming constituents, nitrogen compounds, gravity, and viscosity. Thus the gas oil fraction may be fed directly to the catalytic cracking process without danger of catalyst fouling. The fuel oil fraction is also now a premium fuel.

The process of the present invention may be further illustrated by the following specific examples.

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Example 1

Bachaquero crude topped at 400° F. was heated 4 hours at 725° F. in a sealed autoclave. The pressure developed under these conditions was about 600 p.s.i.g. The Bachaquero feed had a gravity of 14.1° API, a Conradson carbon of 11.3 wt. percent, a Furol viscosity at 122° F. of 187 SSF and contained 2.3 wt. percent sulfur, 0.38 wt. percent nitrogen, 450 p.p.m. vanadium and 50 p.p.m. nickel. The heat treated feed was mixed with an equal volume of C₆/C₇ naphtha having an Engler distillation range of 107° to 191° F. and a gravity of 77.7° API. Approximately 500 cc. of the mixture were placed in an electrical precipitator consisting of an outer stainless steel cylindrical vessel of 78 mm. I.D. as the anode and a concentric stainless steel finger of 34 mm. O.D. as the cathode. A D.C. potential of 1500 volts was applied across the electrodes. Thus the D.C. electrical field is about 680 volts per centimeter. Within the limitations of the equipment there was no indicated current, i.e. any current consumed was less than 0.5 milliamperere. After five minutes there was a copious precipitate collected on the cathode which was spongy and readily sluffed off. Oil was removed from the precipitate by washing with a small volume of the naphtha. The recovered oil amounted to 91% of the original feed and had a gravity of 17.9° API and contained 96 p.p.m. vanadium and 15 p.p.m. nickel.

Example 2

The same Bachaquero topped crude described above after heat soaking for four hours at 750° F. was diluted with three volumes of the light naphtha described above. The mixture was subjected to electrical treatment before and after saturation with anhydrous HCl gas. The electrical treatment was carried out in a stainless steel cylinder of 54 mm. I.D. as the anode with a concentric stainless steel finger of 34 mm. O.D. as the cathode. After electrical treatment for five minutes at 1500 volts (D.C. electrical field of 1,500 volts per centimeter) the precipitate was deposited on the cathode. The amount of current consumed was less than that detectable by the instruments used. The following analyses on the recovered oil show the degree of metals removal effected:

Additive	P.p.m. Vanadium	P.p.m. Nickel
3/1 Naphtha.....	27	8
3/1 Naphtha+HCl.....	14	3

Example 3

Under the same conditions used in Example 2 no deposition was observed if the Bachaquero topped crude had not been heat soaked before solvent addition and electrical treatment.

Also treatment of the heat-soaked feed with A.C. potential using as high as 10,000 volts caused no deposition of precipitate. Also this treatment did not show coagulation of the precipitate as evidenced by the settling rate in comparison with the same mixture not treated with A.C. potential.

The process of the present invention may be modified in many respects. Thus, it may be desirable in some cases to carry out the electrical precipitation step without the addition of a solvent, particularly under elevated temperatures.

Example 4

Negligible metals removal was obtained with Bachaquero topped crude which had been heat treated for four hours at 725° F. when the electrical treatment was carried out, in the absence of a solvent, at temperatures below 250° F. The electrical conductivity, however, increased

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rapidly at higher temperatures, as noted in the following tabulation:

Temperature, ° F.:	Current at 1500 v.-milliamperes
Room (80°).....	0
250° F.....	2-4
450° F.....	25-45

At the higher temperature it was found that the current fell off with time and approached the zero value after 45 min. to one hour. These results were obtained with 200 cc. of feed in a 50 mm. I.D. metal cylinder as the anode and 30 mm. O.D. metal cylinder in the center as the cathode.

The separation can further be significantly enhanced, in the absence of a solvent, by carrying out the electrical treatment as rapidly as possible after the thermal treatment and making provision to insure that the oil is not allowed to dissipate the charges induced during the heat treatment step. This latter condition is obtained by insulating the heat treated oil from direct electrical contact with the ground.

What is claimed is:

1. An improved process for upgrading a metallic contaminated residual petroleum fraction including constituents boiling above about 950° F. which comprises subjecting said fraction in liquid phase to an initial thermal treatment at a temperature of from about 600° to about 900° F. for a period of about 0.3 to about 10 hours under pressures sufficient to maintain the material in a substantially liquid state, thereafter subjecting said fraction at elevated temperatures to a D.C. electrical field in the range of about 680 to 10,000 volts per centimeter, and recovering an oil product depleted in metallic constituents.

2. The process of claim 1 wherein said metallic contaminated fraction is diluted with a light hydrocarbon solvent subsequent to said thermal treatment and prior to said electrical treatment.

3. The process of claim 1 wherein an acidic gas is passed into said thermally treated fraction.

4. An improved process for upgrading a metal contaminated petroleum residual oil fraction containing constituents boiling above about 950° F. which comprises heat soaking said fraction in liquid phase at a temperature from about 650° to 850° F. for a period of about 0.3 to 5 hours under pressures sufficient to maintain the material in a substantially liquid state, diluting said heat-treated oil fraction with about 0.3 to 3 volumes of a naphtha fraction, passing said liquid mixture to an electrical precipitation zone, subjecting said mixture to a D.C. electrical field in the range of about 680 to 10,000 volts per centimeter while maintaining a temperature of about 200° to 400° F. within said zone, and separating as a sludge metallic contaminants from said oil fraction.

5. The process of claim 4 wherein an acidic gas is passed into said thermally treated oil fraction prior to said electrical treatment.

6. The process of claim 5 wherein said gas is HCl.

7. The process of claim 1 wherein the D.C. electrical field is in the range of from about 680 to 1,500 volts per centimeter.

8. The process of claim 4 wherein the D.C. electrical field is within the range of about 680 to 1,500 volts per centimeter.

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