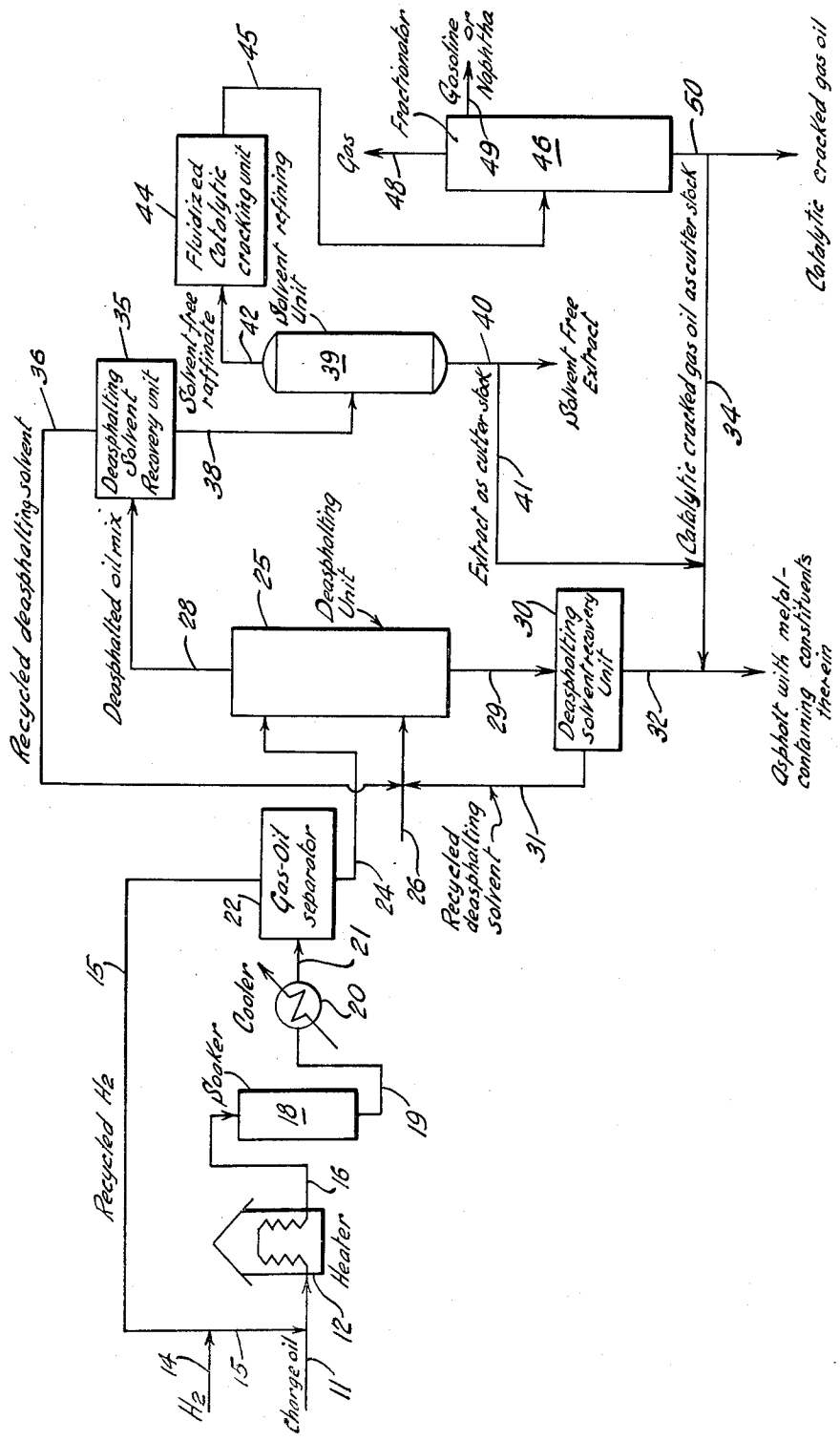
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PETROLEUM TREATING PROCESS

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# PETROLEUM TREATING PROCESS

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This invention relates to the treatment of petroleum for the removal of metal-containing constituents therefrom. More particularly, this invention relates to a method of treating crude oil or a petroleum fraction derived therefrom, such as an asphaltic residuum or a high boiling petroleum fraction, e.g., boiling point above about 700° F., for the removal of metal-containing constituents therefrom, such as the heavy metal-containing constituents.

In accordance with one embodiment the practice of this invention is directed to a method of treating a petroleum fraction or crude containing metal constituents herein to effect removal simultaneously of said metal-containing constituents and upgrading of the oil undergoing treatment. In accordance with still another embodiment of the practice of this invention metal-containing constituents present in a petroleum fraction undergoing treatment are removed together with the other components therein.

Various elements and metals have been found in petroleum. Among the elements and metals which have been detected in petroleum fractions and in crude oil are iron, nickel, vanadium, aluminum, sodium, copper, calcium, magnesium, manganese, barium, silicon, chromium, tin, lead, molybdenum, strontium, cobalt, beryllium, lithium, silver, bismuth, zinc, titanium, rubidium and gold. Most of the above metals, such as gold, silver, etc., are present in trace amounts, e.g., less than about 2 parts per million by weight (p.p.m.) although some such as sodium and the heavy metals such as iron, nickel, vanadium and chromium may be present in relatively substantial amounts, e.g., greater than about 10 p.p.m. These metals are usually not found in elemental form but as components of compounds and complexes forming part of the petroleum fraction or crude oil itself.

Some of these metals are known to be harmful when included in charge stocks to a petroleum refining process, such as a catalytic cracking operation. For example, in a catalytic cracking operation the presence of even relatively minute amounts of heavy metals, such as iron, nickel, vanadium and copper, greatly increase coke and gas yields and reduce gasoline production. Further, these heavy metals also adversely affect the catalyst employed in the catalytic cracking operation. Further, some of these metals such as nickel, chromium and vanadium have been found to be undesirable in petroleum fuels for boilers and gas turbines.

Because of the harmful effects of these metal constituents in crude oils, petroleum fractions and the like, oils containing a substantial amount of these metals have usually not been considered satisfactory for inclusion in the charge to a catalytic cracking unit. Since the metal-containing constituents are relatively high molecular weight and are relatively high boiling materials it has been the practice heretofore to separate the metal-containing constitutents from a crude oil by fractional distillation and by vacuum distillation. There usually results, however, from these operations a fraction of residuum



which is characterized by a relatively high metals content and having a relatively limited usefulness because of its relatively high metal content.

In attempts made heretofore to separate these metal-containing constituents from petroleum one difficulty encountered has been the actual separation of these materials, when precipitated, from the petroleum itself. It has been suggested heretofore to effect separation of these metal-containing constituents by filtration and by settling. It has also been suggested to effect removal of the metal-containing constituents from a treated oil by absorption on porous contact material. None of these methods proposed heretofore have been completely satisfactory. Filtration and settling is time consuming, due particularly to equipment limitations and equipment failures. Absorption is also time consuming.

Accordingly, it is an object of this invention to provide an improved method of treating a petroleum fraction or crude oil for the removal of metal-containing constituents therefrom.

Another object of this invention is to provide an improved method for effecting the separation of solid metal-containing constituents from a liquid petroleum fraction.

Still another object of this invention is to provide an improved method for treating a liquid petroleum fraction and the like wherein removal of solid metal-containing constituents and asphaltic constituents are effected substantially simultaneously.

Yet another object of this invention is to provide an improved method for effecting the separation of solid metal-containing constituents from a liquid petroleum fraction containing the same.

How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure made with reference to the accompanying drawing which schematically illustrates therein an integrated petroleum refining operation including a petroleum treating or conversion process in accordance with this invention for effecting the removal of metal-containing constituents and asphalt from a charge oil. In at least one embodiment of the practice of this invention at least one of the foregoing objects will be achieved.

In accordance with this invention I have provided an improved method for removing metal-containing constituents from admixture with liquid petroleum by contacting the admixture of petroleum and metal-containing constituents carried therein with a liquefied normally gaseous petroleum hydrocarbon. Advantageously the admixture containing petroleum together with the solid metal-containing constituents suspended therein is contacted with the liquefied normally gaseous hydrocarbon under deasphalting or solvent fractionation conditions of temperature and pressure so as to effect substantially simultaneously the removal of the solid metal-containing constituents and any asphaltic and similar high molecular weight bituminous material present in the petroleum undergoing treatment. As a result of contacting the petroleum with a liquefied normally gaseous hydrocarbon the metal-containing constituents together with any asphaltic or high molecular weight bituminous material precipitate and settle out with the resultant formation of two substantially distinct phases, a deasphalted petroleum or oil phase and an asphalt phase containing the metal-containing constituents therein.

Referring now to the accompanying drawing a charge oil, such as an asphaltic petroleum residuum or a petroleum crude, characterized by the presence therein of metal-containing constituents, is introduced via line 11 into a heater 12. Prior to the introduction of the charge oil into heater 12 it is admixed with gaseous hydrogen supplied via lines 14 and 15. At least a portion of the gaseous hydrogen supplied via lines 14 and 15 into

contact with the charge oil in line 11 may be supplied from hydrogen recovered and recycled in the petroleum refining process described herein.

The admixture of charge oil and hydrogen is heated within heater 12 to a suitable elevated temperature, such as a temperature of at least about 500° F., usually in the range 600° F.–850° F., more or less, and at a suitable elevated pressure, such as a pressure in the range 500–5,000 p.s.i.g. The resulting heated admixture of oil and hydrogen is recovered from heater 12 via line 16 and introduced into soaker 18 wherein the heated admixture is permitted to remain for a sufficient period of time to effect the more complete reaction between the hydrogen and the charge oil undergoing treatment. The period of time necessary to effect this more complete reaction between the hydrogen and the charge oil varies depending upon the charge oil employed and the amount of metal-containing constituents in the charge oil, and might vary in the range 1 minute to 60 minutes, more or less. Accordingly the soaker 18 might be eliminated if the residence time of the heated admixture within heater 12 is sufficient to permit the hydrogenation reaction therein to go to substantial completion.

During the above-indicated hydrogenation operation the metal-containing contaminants or constituents in the charge oil undergoing treatment are in effect separated therefrom as substantially solid materials. These solid metal-containing constituents remain suspended within the treated charge oil and are carried along therewith into soaker 18.

The admixture of treated charge oil and metal-containing constituents is recovered from soaker 18 via line 19 and passed through cooler 20 and introduced via line 21 directly into gas-oil separator 22 wherein the separation between the gaseous hydrogen and the resulting treated oil containing solid metal-containing constituents therein is effected. The separated gaseous hydrogen is recovered from separator 22 via line 15 and recycled within the process to contact additional fresh charge oil. The resulting treated oil having the metal-containing constituents suspended therein is recovered from separator 22 via line 24 and introduced into deasphalting unit 25. If desired, or necessary, all or a portion of the separated treated oil may be returned to heater 12, by means not shown, to effect a more complete hydrogenation reaction and precipitation of the metal-containing constituents therefrom.

The solvent deasphalting unit may comprise a batch operation, multiple vessel operation or a substantially continuous liquid-liquid countercurrent treating operation, as indicated in the drawing, wherein the treated oil having metal-containing constituents suspended or entrained therein is introduced via line 24 into the upper portion of deasphalting tower 25 and flowed in countercurrent liquid-liquid contact with a suitable liquid deasphalting solvent, such as a liquefied normally gaseous hydrocarbon, e.g., ethane, propane, n-butane, isobutane, the butylenes and the like or mixtures thereof. The liquid deasphalting solvent is introduced into the lower portion of deasphalter 25 via line 26.

The deasphalting operation is carried out at any suitable deasphalting temperature and pressure, the temperature and pressure being adjusted so as to maintain the deasphalting solvent in the liquid phase during the deasphalting operation. A deasphalting temperature in the range 150–325° F., preferably about or just below the critical temperature of the deasphalting solvent, usually not more than 75 degrees Fahrenheit below the critical temperature of the deasphalting solvent, and a pressure in the range 200–1000 p.s.i.g., and a solvent to charge oil volume ratio in the range 2–10, are employed depending upon the composition of the deasphalting solvent and to some extent the composition of treated oil undergoing deasphalting or solvent fractionation. The deasphalting tower 25 may be operated under substantially isothermal conditions or under a temperature gradient, i.e., top tower temperature greater than bottom tower temperature such as by not more than about 40 degrees Fahrenheit. The deasphalting tower 25 may be operated so that the treated oil undergoing solvent fractionation and/or deasphalting therein is introduced thereinto at a number of points along the height of the tower. Also the deasphalting solvent may be introduced into deasphalting tower 25 at a number of points along the height of the tower.

By contacting the hydrogenated oil which contains relatively finely divided solid metal-containing constituents therein with a liquid normally gaseous hydrocarbon, as in a deasphalting operation, the separation of the finely divided metal-containing constituents from the treated hydrogenated oil is readily and expeditiously effected. The solid metal-containig contaminants suspended within the treated oil introduced via line 24 into deasphalting unit 25 are readily separated therefrom together with the asphaltic constituents therein.

Following the solvent fractionation or deasphalting operation within deasphalting unit 25 there is recovered via line 28 a liquid deasphalted oil mix comprising deasphalting solvent and deasphalted oil now having a substantially reduced metals content, particularly as compared with the charge oil introduced into the process via line 11. There is also recovered from deasphalting unit 25 via line 29 a liquid asphalt phase or mix comprising deasphalting solvent together with asphalt or similar high molecular weight bituminous material and substantially all of the metal-containing constituents originally present in the charge oil. This liquid asphalt mix is then treated in deasphalting solvent recovery unit 30 for the recovery of deasphalting solvent therefrom. The recovered deasphalting solvent is removed via line 31 and recycled to deasphalting unit 25 via line 26. The recovered asphalt together with substantially all of the metal-containing constituents originally present in the charge oil is recovered from solvent recovery unit 30 via line 32. Preferably the asphalt is admixed with a suitable cutter stock, such as an aromatic oil, e.g., a catalytic cracked gas-oil or soluble oil supplied via line 34, and recovered as product.

The liquid deasphalted oil mix separated from deasphalting unit 28 is introduced into solvent recovery unit 35, the recovered deasphalting solvent being recycled via lines 36 and 26 for use in deasphalting unit 25. The resulting deasphalted oil, now having a substantially reduced metals content and substantially free of deasphalting solvent, is recovered from solvent recovery unit 35 via line 38 and introduced into solvent refining unit 39.

Within solvent refining unit 39 the deasphalted oil is contacted with a liquid selective solvent for aromatic hydrocarbons, such as furfural. The solvent refining unit might utilize any suitable device for effecting liquid-liquid contact between the partially immiscible selective solvent employed and the deasphalted oil undergoing treatment. Preferably the solvent refining unit includes an apparatus suitable for effecting continuous liquid-liquid countercurrent contact, such as a packed tower, a centrifugal contactor or a rotating disc contactor.

Various other selective solvents may be employed instead of furfural within the solvent refining unit. Suitable other liquid selective solvents include phenols (Selecto), nitrobenzene, liquid sulfurdioxide, $\beta,\beta'$-dichloroethylether (Chlorex) and dimethylformamide.

There is recovered from solvent refining unit 39 via line 40 a solvent-free extract. If desired, as indicated in the drawing, a portion of this solvent-free extract may be employed as cutter stock via line 41 for admixture with the asphalt recovered from solvent recovery unit 30 via line 32.

There is also recovered from solvent refining unit 39 via line 42 a raffinate now having a substantially reduced

aromatic content and being substantially free of metal-containing constituents (e.g., heavy metals content, vanadium, nickel, iron, copper and the like, less than 5 p.p.m. such as an amount in the range of 0.2–5 p.p.m., more or less), the solvent refining operation also serving to reduce the metal content of the deasphalted oil.

The raffinate is then introduced via line **42** into a fluidized catalytic cracking unit **44** wherein it is contacted with a suitable fluidized cracking catalyst. A suitable cracking catalyst usually comprises an oxide of metals of groups II, III, IV and V of the periodic table, for example, a silica-alumina catalyst containing about 5–30% by weight alumina. The average particle size of the cracking catalyst is usually below about 200 microns, a size sufficient to produce a dense fluidized bed of cracking catalyst.

The resulting gaseous cracked effluent from catalytic cracking unit **44** is introduced via line **45** into fractionator **46** wherein it is fractionated into a gas fraction recovered via line **48**, a gasoline or naphtha fraction recovered via line **49**, and a liquid relatively high boiling fraction, such as a gas oil fraction or gas oil fractions recovered via line **50**. A portion of this heavy gas oil fraction may be recovered as product and employed as fuel or may be supplied via line **34** as cutter stock for the asphalt recovered from solvent recovery unit **30** via line **32**.

The practice of this invention is further illustrated in the following example:

## EXAMPLE 1

In a series of tests oils containing metal-containing constituents therein were treated with hydrogen under various conditions of elevated temperatures and pressures. Table I lists laboratory tests on the metal-containing oils employed in this example. Tables II and III list operating data and product quality tests of the resulting hydrogenated crude oils. Table IV presents data obtained with respect to a hydrogenated heavy paraffin vacuum distillate.

It will be noted that the hydrogenation operation itself removes a substantial amount of the metal-containing constituents from the oil undergoing treatment, including substantially all of the vanadium contained in the heavy crude oil or the heavy vacuum distillate. Essentially complete separation of vanadium is obtained with hydrogenated liquid oil, recoveries as high as 96.0 weight percent of the charge oil being possible.

*Table I*

| Tests | Charge Oils | | | |
|---|---|---|---|---|
| | Mara Crude I | Mara Crude II | San Ardo Crude | Heavy Paraffin Distillate |
| Gravity, ° API | 29.0 | 26.1 | 12.1 | 18.5 |
| Vis., cs. @ 130° F | 11.13 | 17.51 | 748 | ---------- |
| Vis., cs. @ 210° F | 4.57 | 5.79 | 107.6 | 42 |
| ASTM Distillation, ° F.: | | | | |
| IBP | 162 | -------- | 426 | 388 |
| 10% Rec | 288 | -------- | 542 | 642 |
| 50% Rec | 664 | -------- | 705 | 746 |
| End Point | 752 | -------- | 730 | Cracked |
| Vanadium, p.p.m | 220 | 220 | 100 | 40 |
| Nickel, p.p.m | 15 | 15 | 64 | 11 |
| Iron, p.p.m | 5 | 5 | 31 | 15 |
| Carbon Residue, percent wt | 5.8 | -------- | -------- | ---------- |

*Table II*

OPERATING DATA WITH MARA CRUDE [1]

| | Tests | | | | | |
|---|---|---|---|---|---|---|
| | A | B | C | D | E | F |
| Operating Conditions: | | | | | | |
| Temperature, ° F | 700 | 700 | 700 | 700 | 700 | 750 |
| Pressure, p.s.i.g | 685 | 1,000 | 1,500 | 2,000 | 3,000 | 4,600 |
| Hydrogen Rate, cu. ft./bbl | 142.2 | 192.2 | 169.8 | 440.0 | 657.0 | 1,073.0 |
| Yields, Basis Charge: | | | | | | |
| Treated Liquid, Wt. percent | 92 | 91.8 | 95 | 94.0 | 96.0 | 90.0 |
| Solid Residue (predominantly metal-containing constituents) Wt. percent | 4.3 | 4.3 | 5 | 5.0 | 3.7 | 1.0 |
| Hydrogen Consumption, cu. ft./bbl | 4.2 | 86.2 | 76.8 | 293.0 | 290.3 | 417.0 |
| Product Quality: | | | | | | |
| Treated Oil— | | | | | | |
| Gravity, °API | 30.4 | 30.9 | 30.9 | 34.6 | 34.6 | 39.8 |
| Vis., cs. @ 130° F | 3.72 | -------- | 4.11 | -------- | 3.49 | 1.64 |
| Vis., cs. @ 210° F | 1.86 | -------- | 2.0 | -------- | 1.69 | 0.98 |
| ASTM Distillation, ° F.— | | | | | | |
| IBP | -------- | -------- | -------- | -------- | 160 | 150 |
| 10% Rec | -------- | -------- | -------- | -------- | 302 | 230 |
| 50% Rec | -------- | -------- | -------- | -------- | 556 | 440 |
| End Point | -------- | -------- | -------- | -------- | 700 | 760 |
| Vanadium, p.p.m | 32 | 42 | 32 | 5.6 | less than 0.1 | less than 1.0 |
| Nickel, p.p.m | 4 | 5 | 3 | 0.2 | 0.1 | 3 |
| Iron, p.p.m | 0.8 | 0.8 | 4 | 0.9 | 1.0 | -------- |
| Percent Vanadium Removal | 86 | 81 | 86 | 97.4 | 100 | 100 |
| Solid Residue: | | | | | | |
| Vanadium, p.p.m | -------- | 2,000 | 1,400 | 2,400 | 4,300 | 1,600 |
| Nickel, p.p.m | -------- | 1,200 | 1,200 | 1,300 | 2,200 | 1,300 |
| Iron, p.p.m | -------- | -------- | -------- | -------- | -------- | 3,200 |

[1] Tests A, B, C, D and E are made with Mara Crude I and Test F with Mara Crude II

*Table III*

| | Tests with San Ardo Crude | | |
|---|---|---|---|
| | G | H | J |
| Operating Conditions: | | | |
| Temperature, ° F | 700 | 700 | 750 |
| Pressure, p.s.i.g | 2,000 | 5,000 | 4,550 |
| Hydrogen Rate, cu. ft./bbl | 865.0 | 1,585.0 | 1,175.0 |
| Yields, Basis Charge: | | | |
| Treated Liquid, Wt. Percent | 91.6 | 96.3 | 82 |
| Solid Residue (predominantly metal-containing constituents), Wt. Percent | 1.5 | 1.5 | 1.2 |
| Hydrogen Consumption, cu. ft./bbl | 565.0 | 639.0 | 915.0 |
| Product Quality: | | | |
| Treated Oil— | | | |
| Gravity, ° API | 26.4 | 22.7 | 29.3 |
| Vis., cs. @ 130° F | -------- | 9.35 | 1.93 |
| Vis., cs. @ 210° F | -------- | 3.32 | 1.05 |
| ASTM Distillation, ° F.— | | | |
| IBP | 146 | 180 | 112 |
| 10% Rec | 255 | 354 | 221 |
| 50% Rec | 529 | 649 | 447 |
| End Point | 750 | 760 | 760 |
| Vanadium, p.p.m | 1.0 | 5 | 0.3 |
| Nickel, p.p.m | 7.0 | 12 | 4 |
| Iron, p.p.m | 0.6 | 1.3 | 0.2 |
| Percent Vanadium removal | 99 | 95 | 99.7 |
| Solid Residue: | | | |
| Vanadium, p.p.m | 6,000 | 2,100 | 1,200 |
| Nickel, p.p.m | 2,500 | 1,100 | 2,700 |
| Iron, p.p.m | 1,800 | 2,100 | 1,700 |

*Table IV*

TESTS WITH HEAVY PARAFFIN VACUUM DISTILLATE

| | Tests | |
|---|---|---|
| | K | L |
| Operating Conditions: | | |
| Temperature, ° F | 700 | 750 |
| Pressure, p.s.i.g | 2,000 | 5,000 |
| Hydrogen Rate, cu. ft./bbl | 663.0 | 1,105 |
| Yields, Basis Charge: | | |
| Treated Liquid, Wt. Percent | 95.6 | 96 |
| Solid Residue (predominantly metal-containing constituents), Wt. Percent | 3 | 2.5 |
| Hydrogen Consumption, cu. ft./bbl | 253 | 410.0 |
| Product Quality: | | |
| Treated Oil— | | |
| Gravity, ° API | 27.4 | 33.1 |
| Vis., cs. @ 130° F | | 3.12 |
| Vis., cs. @ 210° F | | 1.62 |
| ASTM Distillation, ° F.— | | |
| IBP | 146 | 128 |
| 10% Rec | 365 | 258 |
| 50% Rec | 755 | 581 |
| End Point | 760+ | 760+ |
| Vanadium, p.p.m | 0.5 | 0.7 |
| Nickel, p.p.m | 0.5 | less than 0.02 |
| Iron, p.p.m | 3.0 | 0.9 |
| Percent Vanadium removal | 99 | 98 |
| Solid Residue: | | |
| Vanadium, p.p.m | 1,400 | 1,400 |
| Nickel, p.p.m | 3,000 | 850 |

Petroleum fractions containing heavy metal-containing constituents associated therewith and comparable to the treated hydrogenated oils described hereinabove were treated with liquid isobutane as a deasphalting solvent, employing a solvent-oil volume ratio 5:1, at various temperatures in the range 200–275° F. and at a pressure in the range 200–500 p.s.i.g. The results of these operations are set forth in accompanying Table V.

*Table V*

| Solvent | Deasphalting | | Deasphalted Oil | | | | |
|---|---|---|---|---|---|---|---|
| | Temp., ° F. | Press., p.s.i.g. | Yield, Wt. percent | Carbon Residue, percent | p.p.m. Fe | p.p.m. Ni | p.p.m. V |
| Charge Oil | | | | 26 | 80 | 150 | 350 |
| Isobutane | 200 | 230 | 46.0 | 5.9 | 6 | 11 | 9 |
| Do | 235 | 335 | 40.1 | 5.0 | 6 | 8 | 5 |
| Do | 245 | 385 | 42.0 | 4.1 | | | |
| Do | 270 | 475 | 35.6 | 3.0 | 8 | 3 | 3 |

As indicated by the foregoing test data, there is recoverable from the solvent deasphalting operation carried out in accordance with this invention a hydrogenated solvent deasphalted oil having a very low metals content, in the range 5–25 p.p.m. and lower, as compared with the original charge oil which had a metals content in the range 75–250 p.p.m. The metal-containing constituents originally present in the charge oil are removed in the solvent deasphalting operation together with the asphalt or high molecular weight bituminous constituents originally in the charge oil.

A high boiling petroleum fraction comparable to the deasphalted oil recovered from the aforesaid solvent deasphalting operation was subjected to liquid-liquid contact with liquid furfural and a solvent dosage in the range 75–200% volume, e.g., 125%, basis oil charge. The raffinate resulting from the foregoing furfural solvent refining operation possessed a significantly lower metals content, below about 5 p.p.m., sufficiently low to be considered substantially free of metal-containing constituents.

As indicated hereinabove, this deasphalted, substantially metal-free raffinate is particularly suitable as a charge stock to a catalytic cracking operation since the charge stock is substantially free of metals, particularly metals such as vanadium which tend to deactivate the cracking catalyst.

The hydrogenation operation for the initial treatment of the metal-containing charge oil may be carried out in the presence of a suitable hydrogenation catalyst, preferably a sulfide-resistant hydrogenation catalyst. Suitable hydrogenation catalysts are known and include such catalysts as nickel tungsten sulfide and cobalt molybdate. The catalyst, if employed during the hydrogenation operation, may be in the form of a fixed bed or entrained or suspended in the charge oil undergoing hydrogenation, suitable means being provided for the separation of the catalyst from the resulting hydrogenated oil having the metal-containing constituents suspended therein.

As will be apparent to those skilled in the art many changes, modifications and substitutions are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A method of treating an asphaltic petroleum fraction having metal-containing constituents therein which comprises contacting said petroleum fraction with hydrogen under conditions such that hydrogen reacts with said petroleum fraction to produce an admixture comprising a liquid hydrogen-treated oil characterized by a reduced metal content and containing solid metal constituents suspended therein, subjecting said admixture to contact with a liquid normally gaseous hydrocarbon under deasphalting conditions of temperature and pressure to effect separation of asphaltic or similar high molecular weight bituminous constituents from said treated oil together with said solid metal constituents and recovering from the aforesaid operation a liquid deasphalted oil mix comprising deasphalted treated oil having a reduced amount of said asphalt or bituminous and said metal containing constituents therein and a liquid asphalt mix comprising asphalt or said high molecular weight bituminous constituents admixed with said metal constituents.

2. A method in accordance with claim 1 wherein said normally gaseous hydrocarbon is a $C_4$ hydrocarbon.

3. A method in accordance with claim 1 wherein said normally gaseous hydrocarbon is isobutane.

4. A method in accordance with claim 1 wherein said normally gaseous hydrocarbon is propane.

5. A method in accordance with claim 1 wherein said normally gaseous hydrocarbon is n-butane.

6. A method in accordance with claim 1 wherein the hydrogenation opeartion is carried out under conditions such that the petroleum fraction undergoing treatment is contacted with hydrogen in an amount in the range 10–1000 standard cubic feet per barrel of petroleum fraction undergoing treatment.

7. A method in accordance with claim 1 wherein said hydrogenation operation is carried out at a temperature in the range 700–850° F. and a pressure in the range 2000–5000 p.s.i.g.

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