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SOLVENT DEASPHALTING PROCESS

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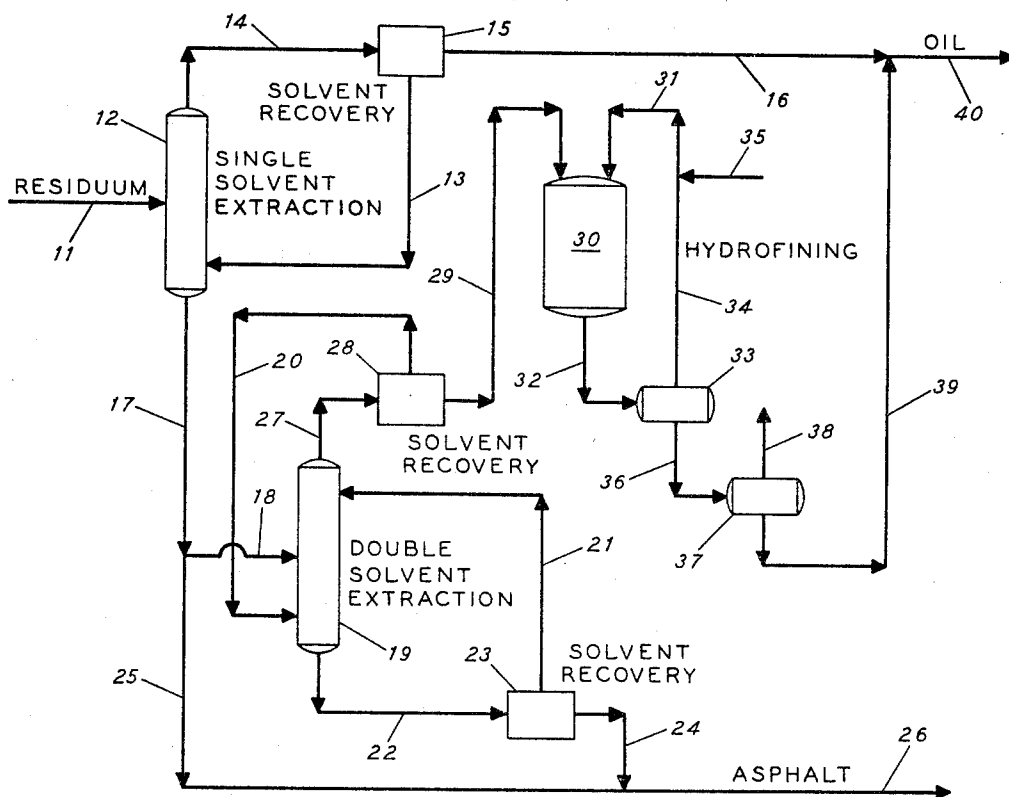


FIG. 1

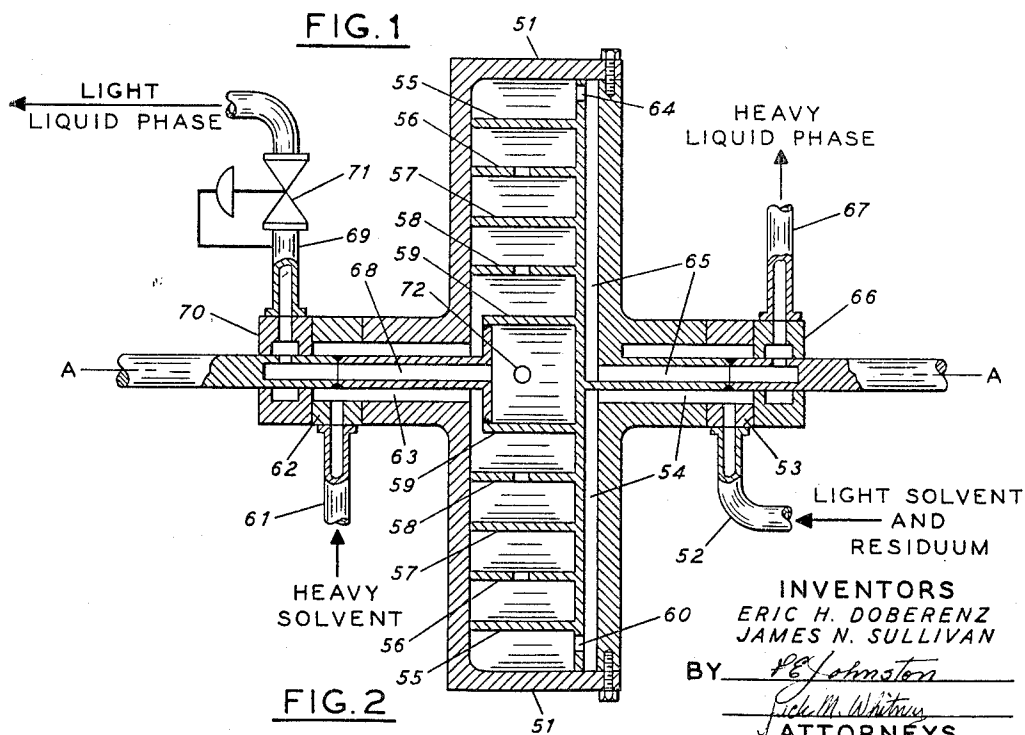


FIG. 2

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## SOLVENT DEASPHALTING PROCESS

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9 Claims. (Cl. 208—45)

This invention relates to the solvent treating of asphaltic materials such as petroleum residuum, and more particularly it relates to the recovery of crackable oil values from residuum by multiple-solvent extraction.

In the refining of crude petroleum a variety of thermal and catalytic processes are available for converting the lower boiling distillate portion into more valuable products. Although only materials boiling below about 750° F. are recovered in the distillate portion by atmospheric distillation, the recoverable distillate portion may include materials boiling up to 950–1150° F., or higher, when vacuum distillation or residuum stripping or similar processes are used. The remaining highest boiling portion, or residuum, generally contains high concentrations of high molecular weight organic compounds of sulfur, nitrogen, oxygen, metals, and other non-hydrocarbon species, as well as high molecular weight hydrocarbons including condensed-ring aromatics. The non-hydrocarbon compounds are often poisonous to certain catalysts, metal compounds being particularly deleterious to cracking catalysts.

The residual portion of crude petroleum is sometimes described in terms of relative solubility as comprising (1) a pentane soluble oil fraction resembling the distillate portion except for its higher molecular weight and boiling point, (2) a less soluble resin or maltene fraction, and (3) an insoluble asphaltene fraction. "Asphaltenes" is used herein in its accepted meaning as referring to that portion which is insoluble when residuum is extracted with 20 volumes of normal pentane. When so extracted with pentane, the asphaltenes separate as solid particles or granules. "Resins" and/or "maltenes" are less clearly defined terms in the art, used herein to describe that portion other than asphaltenes which contain metal compounds; as distinguished from the "oil" portion, which is metal-free but usually contains other hetero-organic compounds. The term "asphaltic constituents" is used herein to refer collectively to the asphaltenes and metal compounds.

The metal-containing organic compounds are distributed in the resin-maltene portion and in the asphaltene portion, though they are found in higher concentrations in the latter. Heretofore, solvent extraction processes applied to residuum for the purpose of recovering crackable oil have been limited to recovering only the oil portion, because metal contamination appears in the oil extract when resins or maltenes are also recovered and because under such conditions a portion of the asphaltenes also appears in the extract, as certain resins appear to carry asphaltenes with them by weak chemical or physical attraction, bonding, or adsorption. The present invention permits recovering as crackable oil a portion of the resins or maltenes in addition to the oil portion, while excluding asphaltenes. In the absence of asphaltenes the metal contaminants can be readily removed from the maltenes-resins and oil by further treatment such as catalytic hydrogenation.

It is known that oil values can be recovered from the residuum boiling above 950° F. by solvent extraction with a light normally-gaseous paraffin solvent such as propane or butane or a mixture thereof, for example by propane deasphalting. Elevated pressure is used in contacting equipment to maintain the propane liquid, and a temper-

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ature near the critical is used to improve solvent selectivity. The oily constituents dissolve in the solvent or extract phase, while asphaltic constituents are rejected by the solvent and remain in the raffinate phase. From a typical residuum boiling entirely above 1000° F. only a low yield of oil is recovered, generally below 40% of the residuum. If high ratios of solvent to residuum are used to obtain oil yields above about 60%, excessive amounts of metal compounds and some asphaltenes appear in the extract phase. This is to be avoided because, generally, the oil recovered by propane deasphalting is fed to a catalytic cracking process, wherein it is particularly desired that the oil contain not over about 4 p.p.m. metals, and preferably not over 0.5 p.p.m. metals, to avoid deactivating the catalyst. Also, a separate solid asphaltene phase may appear in the raffinate, causing plugging in the contacting equipment and making the raffinate difficult to pump or otherwise transport and further process.

This invention provides a new process for recovering additional oil values from asphaltic residuum by extraction wherein the formation of a solid phase is avoided. In accordance with the invention, asphaltic residuum is extracted simultaneously with a light solvent comprising a normally-liquid paraffin and with a heavy solvent comprising aqueous phenol, whereby a light liquid phase comprising predominantly said light solvent and nonasphaltic constituents of said residuum separates from a heavy liquid phase comprising predominantly said heavy solvent and asphaltenes contained in said residuum, recovering from said light phase a deasphalted oil and recovering from said heavy phase an asphaltene concentrate.

In a preferred embodiment of the invention the residuum is extracted in a treating zone wherein said solvents flow countercurrent to each other to contact said residuum, which is introduced at an intermediate point.

Preferably the solvents are caused to flow countercurrent to each other to contact the residuum by the combined actions of centrifugal force and density differences in rotating contactor, wherein the heavy solvent comprising aqueous phenol is introduced near the axis and the light liquid phase is withdrawn from a point nearer the axis, and the light solvent comprising normally liquid paraffins is introduced near the periphery and the heavy liquid phase is withdrawn from a point nearer the periphery.

In another embodiment, additional oil is recovered from the asphaltic fraction remaining after recovery of a portion of the oil from residuum by single solvent extraction, by further treating said asphaltic fraction with a light normally-liquid paraffin solvent and with a heavy aqueous phenol solvent.

These and other embodiments will become apparent from the following detailed description and the appended drawings, wherein:

FIG. 1 is a flow diagram indicating diagrammatically the manner in which the invention may be used to recover crackable oil values from an asphaltic fraction; and FIG. 2 is a diagrammatic representation of the manner in which the asphaltic residuum may be extracted with the two solvents in a rotating centrifugal contactor.

The feed to the process of this invention is an asphaltic residuum, i.e., a high boiling hydrocarbonaceous material containing asphaltenes and also containing high molecular weight constituents other than asphaltenes, including metal compounds. Examples of the feeds contemplated are the residuum from atmospheric distillation of crude petroleum, but more particularly the bottoms from vacuum distillation of crude petroleum or the bottoms from the stripping of crude residuum. Also, the feed may be a portion of the highest boiling portion of petroleum from which other constituents have already been

separated by solvent extraction. The feed may be derived from sources other than crude petroleum, and may comprise the heaviest portions of oil obtained from similar materials, such as gilsonite, shale oil, tar sands, and coal, which also contain asphaltene.

In accordance with the invention the feed is contacted simultaneously for extraction with a light solvent and with a heavy solvent. The light solvent selectively dissolves oily and resinous material while rejecting asphaltene and condensed ring aromatic structures and most of the metal-containing compounds. More particularly, the light solvent is a normally-liquid paraffin, in particular a mixture of paraffin hydrocarbons having between 5 and 10 carbon atoms to the molecule. The preferred example of the solvent is alkylate, the isoparaffin-rich light gasoline-boiling-range material produced by reacting an olefin such as butene with an isoparaffin such as isobutane, in the presence of an acidic catalyst such as sulfuric acid or hydrogen fluoride, and distilling to separate the unconverted material and light normally-gaseous by-products and the heavier polymer and alkylation by-products from the alkylate. Thus, the alkylate solvent will be predominantly normal octane and isooctane with lesser amounts of higher boiling and lower boiling paraffins.

The heavy solvent selectively dissolves the asphaltic constituents including asphaltene and most of the heterocyclic metal compounds and a portion of the resinous material, while rejecting oily constituents. In particular, the heavy solvent comprises aqueous phenol, i.e., a solution or mixture of phenol and water containing between 2 and 25 weight percent water, but preferably between 3 and 10 weight percent water.

The light solvent and the heavy solvent are substantially immiscible at the conditions used in the extraction. Although each solvent will dissolve a small portion of the other solvent, particularly in the presence of the residuum feed, the solvents are sufficiently different in nature such that there is a substantial density difference leading to the formation of two distinct liquid phases. Conditions in the extraction are such as to maintain both phases in the liquid condition and to avoid the occurrence of any solid phase. Thus, the temperature in particular is controlled high enough to maintain the material liquid, but low enough to keep the liquid phases immiscible. More particularly, the temperature will generally be in the range between 100 and 400° F., preferably between 100 and 300° F., and most generally in the neighborhood of about 150° F. Atmospheric pressure operation may be used, although somewhat superatmospheric pressures may be desired when higher temperatures are used, to prevent loss of the more volatile light solvent. Thus, although elevated pressures may be used to permit the use of higher temperatures, such elevated pressure operation is not necessary as in the case of propane deasphalting, because the light solvent employed in the invention is normally liquid at atmospheric conditions.

The relative amounts of the respective solvents employed depends on the nature of the asphaltic residuum feed and on the nature of the products desired to be recovered. The preferred use of the invention is to separate an asphaltic residuum into an asphaltene-free oil fraction, which may be further treated to render it suitable as a catalytic cracking feed, and an asphaltene concentrate which may be used as a blending stock for producing asphalt. Preferred feeds are vacuum reduced crude residuum from which a portion of the oily constituents has already been removed by propane deasphalting, or a residuum which has been stripped to remove most of the lower boiling oily constituents. In general, the volume ratio of light solvent to residuum feed is in the range between 1 and 15 volumes of light solvent per volume of feed, but more preferably in a volume ratio between 2 and 10. The ratio of heavy solvent to residuum will generally be in the range between 1 and 10 volumes per volume of feed, but more preferably between 2 and 4.

Thus, the relative ratio of light solvent to heavy solvent will be between 1 and 10 volumes of light solvent per volume of heavy solvent, but more preferably between 1 and 4 volumes of light solvent per volume of heavy solvent.

When the asphaltic feed is contacted with the preferred solvent system, a separation is performed whereby a heavy liquid phase comprising predominantly said heavy solvent and asphaltene separates from a light liquid phase comprising predominantly said light solvent and oily and resinous constituents of the feed, such that from the respective phases there can be recovered an asphaltene concentrate and an asphaltene-free oil.

Referring now to FIG. 1, there is shown an embodiment of the invention comprising a novel processing scheme for separating crude residuum into asphalt and oil suitable for catalytic cracking. The residuum feed, such as the bottoms from vacuum distillation of crude petroleum, passes through line 11 to contacting zone or column 12, wherein it is extracted by a solvent such as upflowing light normally-gaseous paraffins introduced through line 13. For example, the pressure and temperature in column 12 are 400 p.s.i.g. and 200° F., respectively, and the solvent is propane. A mixture of propane and oily constituents of the residuum is taken overhead through line 14 to solvent recovery zone 15, wherein the propane is recovered for reuse in line 13, for example by stripping or distillation, and solvent-free oil is recovered in line 16. From a typical vacuum reduced crude there is recovered in line 16 a yield of about 35 volume percent of oil, free of asphaltene, containing about 4 p.p.m. metals, primarily nickel and vanadium. Although this metal content is near the upper limit, this feed is suitable for catalytic cracking. A lower metal content of about 0.5 p.p.m. would be preferred, but the yield would then be restricted to an uneconomically low percentage. The insoluble raffinate portion of the residuum feed is withdrawn from the bottom of contacting column 12 through line 17. This stream may contain some entrained or dissolved solvent, and ordinarily this small amount of solvent will also be recovered for reuse. As explained hereinafter, however, removal of the solvent is not always essential, and consequently that step has been omitted from FIG. 1.

Since only a portion of the oil values has been recovered from the resinous feed, the material in line 17 still contains some oil, most of the resins, and nearly all of the asphaltene originally present in the residuum. At least a major portion of this asphaltic material is passed through line 18 to countercurrent solvent extraction zone or column 19, wherein it is contacted with an upflowing light solvent, introduced through line 20, and with a downflowing heavy solvent, introduced through line 21. A separate heavy liquid phase thus collects at the bottom of column, tower, or contacting zone 19, which is withdrawn through line 22 and passed to solvent recovery zone 23. The heavy liquid in line 22 comprises predominantly heavy solvent, i.e., phenol and water, and asphaltene originally contained in the feed. A small amount of the light solvent is also dissolved therein. In recovery zone 23, the solvents are separated from the asphaltene, with the heavy solvent being recycled through line 21. The asphaltene is recovered in line 24, and may be blended with the untreated portion of the asphaltic material in line 25 to form an asphalt product recovered in line 26. The product asphalt is thus enriched in asphaltene, thereby improving its properties with respect to use as a paving asphalt.

From extraction zone 19 there is also withdrawn through line 27 the light liquid phase comprising the light solvent and the oily and resinous portions of the residuum from which the asphaltene have been removed. The light solvent is separated from the oil in solvent recovery zone 28 for recycling through line 20. Any solvent which was entrained with the asphaltic feed in

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line 17 will also be recovered in zone 28. These solvents may be the same or quite similar. That is, although propane is not a suitable solvent for use in extraction zone 19, it is contemplated that a solvent such as pentane or hexane, which would be suitable in zone 19, could also be the effective solvent in the first extraction zone 12.

The asphaltene-free oil thus obtained in line 29 preferably comprises a major portion of the material treated. In particular, preferably between 60 and 90 volume percent of the feed in line 18 is recovered in line 29. The solvent ratios and water contents of the phenol-water solvent are so controlled as to achieve this separation. With this high yield it will generally be found that the oil in line 29 has an appreciable metal content such that it would not be suitable for use as feed to a catalytic cracker. In particular, the metal content will generally be above 10 p.p.m. nickel plus vanadium and quite frequently between 100 and 200 p.p.m. metals. When the oil is free of asphaltenes, however, it is found that the metals are quite readily removed by hydrofining or like hydrogenation processes, wherein the metal compounds are broken up and the metals themselves deposit on a porous refractory material, such as the hydrofining catalyst.

Thus, in accordance with this embodiment of the invention, the metals are removed by passing the oil in line 29 into hydrofining reaction zone 30, which contains a hydrofining catalyst such as a metal of Group VIII, preferably cobalt or nickel, together with a metal of Group VI, preferably molybdenum or tungsten, on a porous support such as alumina, silica-alumina, silica-magnesia, or similar materials, but preferably alumina. The catalyst usually contains at least 1% of the Group VIII metal and at least 2% of the Group VI metal. Hydrogen or hydrogen-rich gas is also passed into reaction zone 30 via line 31, in a ratio to oil in line 29 of between 1000 and 10,000 standard cubic feet per barrel. Conditions in reaction zone 30 are controlled generally in the range 0.2-15 LHSV (volumes of oil per volume of catalyst per hour), 300-900° F., and 200-5000 p.s.i.g. More preferred conditions are 1000-8000 SCF H<sub>2</sub>/bbl., 0.3-3 LHSV, 400-800° F., and 800-3000 p.s.i.g., the conditions of severity being adjusted in accordance with the metal content of the oil in line 29. Even with the most highly metal-contaminated oils, however, conditions more severe than represented by a space velocity of about 0.5 LHSV, a temperature of about 775° F., and a pressure of about 2000 p.s.i.g. are rarely required. It will be found that the metal content of an oil containing in the neighborhood of 100 p.p.m. nickel plus vanadium can be reduced to less than 4 p.p.m. by contacting at the last-mentioned severe conditions without excessive coke formation or fouling of the catalyst when the oil is prepared in accordance with the invention. In contrast thereto, when an oil containing 100 p.p.m. metals was prepared by propane deasphalting a vacuum reduced crude to obtain a high yield of deasphalted gas oil of about 75%, containing 100 p.p.m. metals, the oil also contained a significant amount of asphaltenes. When hydrofined with a nickel-molybdenum-alumina catalyst which had been found to be particularly active for metals removal, it was found that the metal content could not be reduced to below 10 p.p.m. even at the aforementioned severe conditions. It is believed that the asphaltenes present interfered with the hydrogenation reaction and also acted to deactivate the catalyst and caused rapid coking or fouling.

From hydrofining reaction zone 30 of FIG. 1 the reactor effluent mixture passes through line 32 to high pressure separator 33, wherein hydrogen-rich gas is separated for recycle through line 34, in admixture with makeup hydrogen added through line 35, back to the reactor via line 31. The separated oil phase passes through line 36 to another separator 37, preferably at a lower pressure, wherein dissolved light by-products are flashed off through line 38, and oil sufficiently reduced in metal content to be suitable for use as a catalytic cracker

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feed is recovered in line 39. This oil can be blended with the low yield of low metal content oil in line 16 to form a major portion of the feed to a catalytic cracker in line 40.

Referring now to FIG. 2, there is shown diagrammatically and in cross section the use of a centrifugal contactor for carrying out the double solvent extraction of this invention, which has the advantage of providing intimate contacting of the feed with the solvents with accelerated separation of the liquid phases, whereby a high flow rate of residuum may be treated continuously in equipment occupying a relatively small space. The apparatus itself forms no part of this invention, but the use of equipment operating in principle as illustrated to treat residuum with two solvents simultaneously is an embodiment of this invention. It appears that heretofore solvent extraction of residuum has been carried out only in large contactors and tanks with gravity settling of the phases, even though the advantages of accelerated settling may have been recognized. The problem of the possibility of solids precipitation in a centrifugal device would dictate against considering such equipment. Accordingly, an understanding of how this embodiment of the invention is carried out will best be gained by reference to the operation of typical apparatus which can be used.

There is shown in FIG. 2, in cross section, the rotor 51 of a centrifugal contactor, which is supported and caused to rotate about axis A-A. The asphaltic residuum feed is blended with the light normally liquid solvent, e.g., alkylate, and passed via pipe 52 to the apparatus. The amount of solvent used may be such that a homogeneous solution is formed in pipe 52, but usually there will be two liquid phases, which can be satisfactorily pumped. There may even be separation of a solid asphaltene phase, which, however, presents no problem as the slurry is dilute enough that this can also be readily pumped. Pipe 52 communicates with interior conduit or passageway 54 through mechanical seal 53, so constructed that rotor 51 is free to rotate while pipe 52 and seal 53 are stationary. Within rotor 51 are several concentric rings, generally more than the five shown identified by numerals 55-59, forming concentric annular compartments wherein liquid-liquid contacting occurs. Each ring has at least one opening, and the openings are staggered to compel circumferential as well as radial countercurrent liquid flow between compartments. For example, ring 56 has two openings 180° apart, and the openings in rings 55 and 57 are displaced 90° relative to the openings in ring 56. Hence, the openings in odd-numbered rings are aligned with opening 72 in ring 59. Liquid in conduit 54 passes into one of the compartments through an opening, such as 60 near the periphery of rotor 51 but spaced a significant distance from the periphery. Similarly, heavy solvent, e.g., phenol-water, is introduced via pipe 61, through mechanical seal 62, into interior conduit or passageway 63. Conduit 63 terminates in an opening into a compartment near the axis but spaced a significant distance therefrom. The centrifugal force generated by the rotation of rotor 51 tends to force all of the material to the periphery, but the greater density of the liquid phase comprising predominantly heavy solvent causes it to occupy the space nearest the periphery and to thereby force the lighter liquid phase toward the axis. A layer of light liquid builds up on the outer surface of each ring, and a layer of heavy liquid builds up on the inner surface of each ring, until sufficient head is formed to cause the liquids to pass countercurrently through an opening into the next compartments. Heavy liquid droplets are thrown radially outward until they coalesce on the inner surface of the next ring, pass through another opening, and so on, finally collecting at the periphery. Light liquid droplets are displaced through an opening, continue radially inward, coalesce, pass through another opening, and so on, finally collecting at the axis. The heavy liquid phase is withdrawn from the periphery through opening 64 into

conduit 65, communicating with exterior pipe 67 through mechanical seal 66. The light liquid phase collecting near the axis overflows through conduit 68 into exterior line 69, communicating through seal 70. The operation of the unit to insure a phase separation therein may be controlled, for example as shown, by means of back pressure control valve 71 restricting the rate of withdrawal of the light liquid phase.

#### Examples 1 through 6

The following examples present data indicating the effects of certain variables in the solvent extraction process of the invention, using the preferred solvent system of alkylate and phenol-water, in the treatment of bottoms streams from residuum stripping of reduced crude petroleum. The extractions were carried out in a centrifugal contactor (Podbelniak) operating in principle substantially as shown in FIG. 2, with 18 stages, a rotor diameter of 18", and operating at 3000 r.p.m. The extractions were carried out in a continuous manner until stable equilibrium conditions were achieved, whereupon the relative amounts of light liquid phase and heavy liquid phase were measured. The oil product recovered from the light liquid phase and the asphaltic product recovered from the heavy liquid phase were analyzed. In this examples the primary variables were the relative amounts of alkylate and phenol-water solvents employed, the ratio of the respective solvents to the feed, and the water content of the phenol-water solvent. The conditions used and the results obtained are summarized in the following Tables I and II.

In typical preferred operation, as in Example 1, the light liquid phase contained 71% alkylate, 15% phenol-water, and 14% oil, by weight; while the heavy liquid phase contained 78% phenol-water, 14% alkylate, and 8% asphaltic constituents, prior to separation of the solvents and recovery of the products.

#### Supplementary experiments

In other experiments the residuum stripper bottoms feed was extracted in the centrifugal contactor only with a single solvent, alkylate, in a ratio of 10 volumes per volume of residuum. The alkylate was introduced near the periphery and the residuum was introduced near the axis. No phase separation occurred, in that it appeared that any asphaltenes which separated did so near the rotor axis and were not sufficiently more dense than the alkylate to be carried to the periphery countercurrent to the high flow rate of alkylate.

In another experiment the residuum feed was diluted with 10 volumes of alkylate, and the mixture was then fed to the centrifugal rotor near the periphery. A solid asphaltene phase separated, which gradually clogged the rotor with solids causing pressure fluctuations, surging, and unstable operation.

In another experiment, the residuum feed was diluted with an aromatic solvent comprising a mixture of ortho-, meta-, and para-xylenes. The diluted feed was then mixed with 10 volumes of alkylate and fed to the centrifugal contactor. No solid clogging occurred, but the heavy liquid phase withdrawn from the rotor periphery and the light liquid phase withdrawn from the rotor axis

TABLE I

| Example.....                                                 |       | 1           |                   | 2           |                   | 3           |                   |
|--------------------------------------------------------------|-------|-------------|-------------------|-------------|-------------------|-------------|-------------------|
| Treating Conditions:                                         |       | 5.43        |                   | 2.79        |                   | 3.57        |                   |
| Alkylate/Feed, Volume Ratio.....                             |       | 2.86        |                   | 2.28        |                   | 2.72        |                   |
| Phenol-Water/Feed, Volume Ratio.....                         |       | 9.2         |                   | 5.6         |                   | 14          |                   |
| Water in Phenol-Water, vol. percent.....                     |       | 160         |                   | 160         |                   | 160         |                   |
| Temperature, ° F.....                                        |       |             |                   |             |                   |             |                   |
|                                                              | Feed  | Oil Product | Asphaltic Product | Oil Product | Asphaltic Product | Oil Product | Asphaltic Product |
| Inspections:                                                 |       |             |                   |             |                   |             |                   |
| Gravity, ° API.....                                          | 6.1   | 9.4         | -4.1              | 11.3        | -0.4              | 8.5         | -4.6              |
| Viscosity at 275° F.....                                     | 1,455 | 1,660       | 2,610             | 1,515       |                   | 1,185       | 2,3,000           |
| Metal Content, p.p.m. Ni+V.....                              | 240   | 107         |                   | 96          |                   | 125         |                   |
| Asphaltene Content, wt. percent.....                         | 10.4  |             | 43                |             | 20                |             | 46                |
| Yield, wt. percent of Feed.....                              |       | 75.6        | 24.4              | 51.4        | 48.6              | 81.8        | 18.2              |
| Asphaltene Recovery, wt. percent of asphaltenes in feed..... |       | (nil)       | 100               | 6.5         | 93.5              | 13.5        | 86.5              |
| Metals Recovery, wt. percent of metals in feed.....          |       | 33.8        | (66.2)            | 20.6        | (79.4)            | 42.5        | (57.5)            |

<sup>1</sup> SSU. <sup>2</sup> SSF.

TABLE II

| Example.....                                                 |       | 4           |                   | 5           |                   | 6           |                   |
|--------------------------------------------------------------|-------|-------------|-------------------|-------------|-------------------|-------------|-------------------|
| Treating Conditions:                                         |       | 10.2        |                   | 8.1         |                   | 10.6        |                   |
| Alkylate/Feed, Volume Ratio.....                             |       | 1.47        |                   | 1.83        |                   | 3.46        |                   |
| Phenol-Water/Feed, Volume Ratio.....                         |       | 13.4        |                   | 10          |                   | 8.5         |                   |
| Water in Phenol-Water, Volume percent.....                   |       | 160         |                   | 170         |                   | 160         |                   |
| Temperature, ° F.....                                        |       |             |                   |             |                   |             |                   |
|                                                              | Feed  | Oil Product | Asphaltic Product | Oil Product | Asphaltic Product | Oil Product | Asphaltic Product |
| Inspections:                                                 |       |             |                   |             |                   |             |                   |
| Gravity, ° API.....                                          | 5.9   | 6.8         | -6.5              | 7.4         | -5.2              | 8.6         | -4.3              |
| Viscosity at 275° F, SSU.....                                | 1,851 | 1,270       |                   |             |                   | 801         |                   |
| Metal Content, p.p.m. Ni+V.....                              | 287   | 149         |                   | 213         |                   | 115         |                   |
| Asphaltene Content, wt. percent.....                         | 11.6  |             | 77                |             | 57                |             | 56                |
| Yield, wt. percent of Feed.....                              |       | 94.7        | 5.3               | 81.7        | 18.3              | 78.9        | 21.1              |
| Asphaltene Recovery, wt. percent of asphaltenes in feed..... |       | (65)        | 35                | (10)        | 90                | (nil)       | 100               |
| Metals Recovery, wt. percent of metals in feed.....          |       | 49          | (51)              | 60.5        | (39.5)            | 31.6        | (69.4)            |

NOTE: Figures in parentheses were calculated by difference.

had substantially the same composition, indicating that the system was completely miscible. Similar results were obtained when anhydrous phenol was used as the heavy solvent and alkylate as the light solvent.

From the foregoing examples and supplementary experiments, it is seen that the use of aqueous phenol as the heavy solvent was necessary to obtain two liquid phases of substantially different density and composition. As the water content of the aqueous phenol solvent is increased, the heavy solvent rejects first the oily constituents, then the resins or maltenes and organo-metallic compounds, and then the asphaltenes, respectively with increasing water content (Examples 2, 5, and 3). This corresponds to the order of preferred solubility of the compounds in the light alkylate solvent phase; that is to say, the alkylate preferentially rejects these classes of compounds in the reverse order. However, if a low ratio of alkylate to feed is used, and/or the water content of the phenol is too high, selectivity is poor because the aqueous phenol of high water content rejects the resins or maltenes and metal compounds more strongly than does the alkylate (Example 3). Likewise, if too great a volume of alkylate is used, the light alkylate solvent phase begins to extract asphaltenes from the heavy aqueous phenol solvent phase (Example 4).

Hence, the preferred solvent dosages are such as to provide a volumetric ratio of alkylate to aqueous phenol between 1 and 4 volumes per volume and a total solvent dosage between about 4 and 13 volumes of total alkylate and aqueous phenol per volume of residuum feed. Thus, for example, the preferred dosages are between 2 and 4 volumes of aqueous phenol per volume of residuum and between 2 and 10 volumes of alkylate per volume of residuum. The water content of the aqueous phenol solvent is preferably between 3 and 10% by weight. The preferred conditions are selected so that a yield of between 60% and 90% by weight of deasphalted oil is recovered in the light liquid phase, and the asphaltene concentrate recovered from the heavy liquid phase contains substantially all of the asphaltenes in the feed and most of the metal compounds. Thus, in the preferred embodiment of the invention, the asphaltene fraction and the oil fraction of the residuum are completely segregated in separate liquid phases, most of the resin-maltene fraction is recovered with the oil fraction, and only these resins and maltenes as are attractively bonded to the asphaltenes are rejected from the oil fraction.

From the foregoing description, of the invention, the examples, and the preferred method of using it, it is apparent that many changes and modifications could be made therein without departing from the spirit of the invention, and such changes and modifications as fall within the appended claims are intended to be embraced thereby.

We claim:

1. The process which comprises extracting an asphaltic residuum simultaneously with a first solvent comprising a normally liquid paraffin having between 5 and 10 carbon atoms to the molecule and in a ratio of between 2 and 10 volumes of said normally liquid paraffin per volume of said residuum and with a second solvent comprising phenol and between 2 and 25 weight percent water, the aqueous phenol being in a ratio of between 2 and 4 volumes of aqueous phenol per volume of residuum, the ratio of said normally liquid paraffin to aqueous phenol being between one and four, in a treating zone at a temperature between 100° F. and 300° F. wherein said solvents flow countercurrent to each other to contact said residuum at conditions whereby formation of a solid phase is avoided and there is obtained a light liquid phase comprising predominantly said first solvent and nonasphaltic constituents of said residuum separate from a heavy liquid phase comprising predominantly said second solvent and asphaltenes contained in said residuum, recovering from said light phase a deasphalten-

ed oil in a yield of between 60 and 90% by volume based on said residuum treated, and recovering from said heavy phase an asphaltene concentrate.

2. The process of claim 1 wherein said solvents are caused to flow countercurrent to each other to contact said residuum by the combined actions of centrifugal force and density differences in a rotating contactor wherein said second solvent is introduced near the axis and said light phase is withdrawn from a point nearer the axis, and said first solvent and residuum feed are introduced near the periphery and said heavy phase is withdrawn from a point nearer the periphery.

3. The process of claim 1 wherein said first solvent is an isoparaffin-rich mixture of paraffin hydrocarbons containing between 5 and 10 carbon atoms to the molecule.

4. The process of claim 1 wherein said asphaltic residuum is the asphaltic fraction remaining after recovery of deasphalted oil from crude residuum by solvent extraction with a liquid normally gaseous hydrocarbon.

5. The process of claim 1 wherein said first solvent is alkylate.

6. A process for producing crackable oil from petroleum residuum containing oil, asphaltenes, and metal compounds, which comprises separating said residuum by solvent extraction with a liquid normally-gaseous hydrocarbon solvent into a major asphaltic raffinate and a minor deasphalted oil extract containing less than 4 p.p.m. metals and suitable for catalytic cracking, separating at least the major portion of said asphaltic raffinate by dual solvent extraction simultaneously with a light solvent for oil comprised of a normally liquid paraffin having between 5 and 10 carbon atoms to the molecule and with an immiscible second solvent for asphaltenes comprising aqueous phenol containing between 2 and 25 weight percent water, in a countercurrent extraction zone, recovering a minor asphaltene concentrate from the resulting heavy liquid phase, recovering a major deasphalted oil containing between 10 and 200 p.p.m. metals and unsuited for catalytic cracking from the resulting light liquid phase, and removing metals from said deasphalted oil by catalytic hydrogenation to obtain a deasphalted oil containing less than 4 p.p.m. metals and suitable for catalytic cracking.

7. The process of claim 6 wherein said asphaltic raffinate is extracted by contacting with alkylate in a ratio of between 2 and 10 volumes of alkylate per volume of said raffinate and with aqueous phenol containing between 3 and 10 weight percent water in a ratio of between 2 and 4 volumes of aqueous phenol per volume of raffinate, the ratio of alkylate to aqueous phenol being between one and four, at a temperature between 100° F. and 200° F., to obtain a yield of deasphalted oil between 60 and 90% by volume based on said raffinate treated.

8. The process which comprises contacting reduced crude petroleum residuum, containing oil, asphaltenes, and metal compounds, in a first extraction zone with a solvent comprised of liquid paraffins having between 5 and 10 carbon atoms to the molecule, thereby separating said residuum into:

a raffinate phase, containing a minor amount of said solvent and a major asphaltic portion of said residuum including substantially all the asphaltenes and metal compounds therein,

and an extract phase containing most of said solvent and a minor deasphalted oil portion of said residuum containing less than 4 p.p.m. metals and suitable for catalytic cracking;

recovering deasphalted oil free of said solvent from said extract phase;

passing said raffinate phase including solvent therein to a dual solvent extraction zone and therein contacting it simultaneously and countercurrently with added solvent comprised of liquid paraffins having

- between 5 and 10 carbon atoms to the molecule and with a solvent for asphaltenes comprising aqueous phenol containing between 2 and 25 weight percent water, which solvent is heavier than and immiscible with said solvent comprised of paraffins, thereby separating the asphaltic portion of the residuum into:
- a light liquid phase, containing a major portion of said solvent comprised of paraffins, a minor amount of said heavier aqueous phenol solvent for asphaltenes, and a major deasphalted oil portion of said asphaltic portion containing between 10 p.p.m. and 200 p.p.m. metals and unsuited for catalytic cracking,
  - and a heavy liquid phase, containing a minor amount of said solvent comprised of paraffins, a major portion of said heavier aqueous phenol solvent for asphaltenes, and a minor asphaltene concentrate portion of said asphaltic portion;
  - separately recovering the solvents from said light and heavy phases, and returning a portion of the recovered solvent comprised of liquid paraffins to said first extraction zone;
  - removing metals from the deasphalted oil recovered from said light liquid phase by catalytic hydrogenation to obtain a hydrogenated deasphalted oil containing less than 4 p.p.m. metals and suitable for catalytic cracking;
  - and catalytically cracking said deasphalted oil and the hydrogenated deasphalted oil.
9. The process of claim 8 wherein said solvent comprised of liquid paraffins is comprised predominantly of isoparaffins, and in said dual solvent extraction zone

said raffinate is contacted with said solvent comprised of liquid paraffins in a ratio of between 2 and 10 volumes of solvent per volume of said raffinate and with said aqueous phenol solvent in a ratio of between 2 and 4 volumes of solvent per volume of raffinate, the ratio of paraffin solvent to aqueous phenol solvent being between 1 and 4, at a temperature between 100° F. and 200° F., to obtain a yield of deasphalted oil between 60 and 90 percent by volume based on said raffinate treated.

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