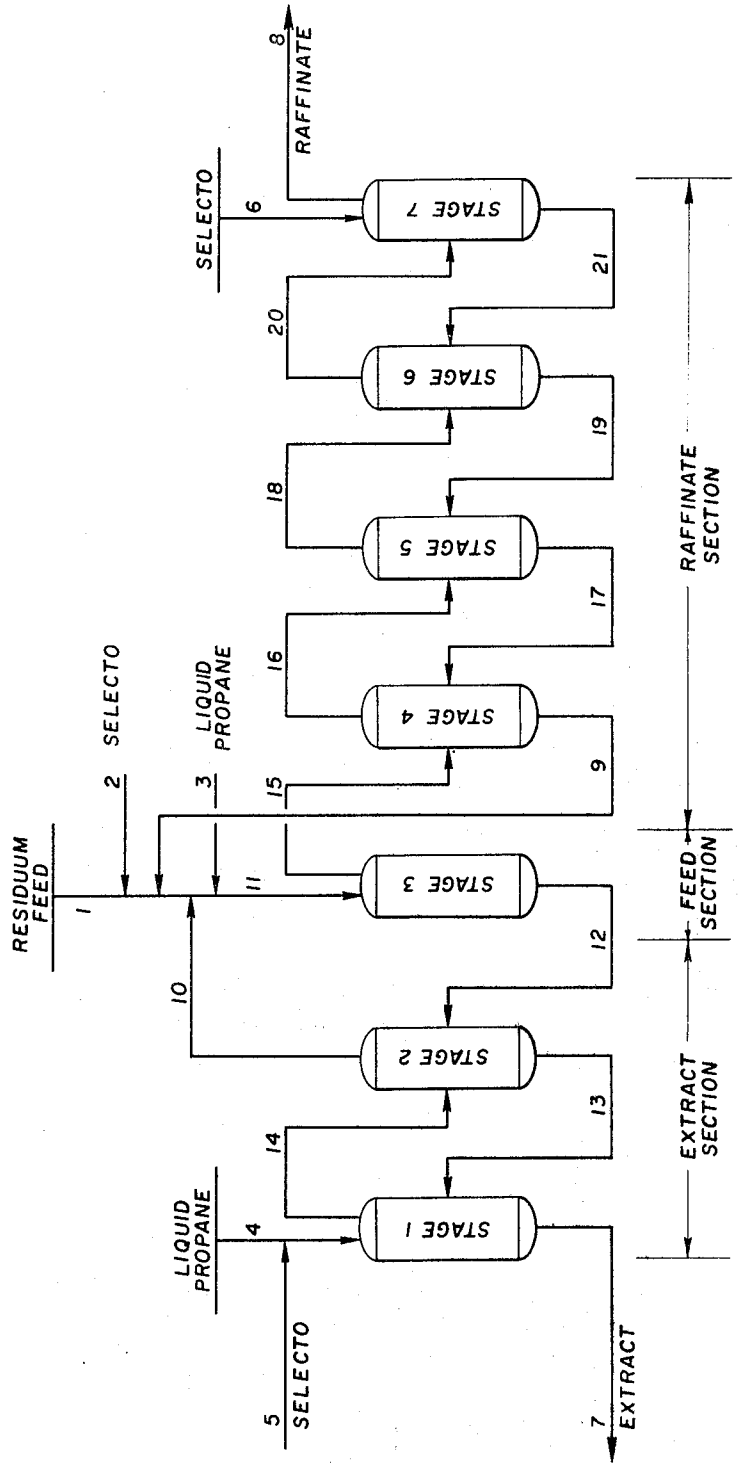
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DUO-SOL PROCESS WITH SPLIT FEED OF POLAR SOLVENT

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INVENTORS

RAYMOND N. FLECK
LOUIS M. DVORACEK
PAUL F. LUETH

BY

Lamar S. Henderson

ATTORNEY

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DUO-SOL PROCESS WITH SPLIT FEED OF POLAR SOLVENT

Raymond N. Fleck, West Covina, Louis M. Dvoracek, Brea, and Paul F. Lueth, Fullerton, Calif., assignors to Union Oil Company of California, Los Angeles, Calif.

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ABSTRACT OF THE DISCLOSURE

A Duo-Sol process wherein a residuum is subjected to a countercurrent liquid-liquid extraction process utilizing a paraffinic solvent to extract paraffins and a polar solvent to extract aromatics, naphthenes and asphaltenes is improved by introducing 5–50 percent of the polar solvent into the residuum feed stage. In another emobdiment, 1–5 percent of the polar solvent is introduced into the paraffinic solvent feed stage. The invention is particularly useful wherein the residuum contains a relatively high amount of asphaltenes.

BACKGROUND AND OBJECTS OF THE INVENTION

The invention relates to an improvement in a Duo-Sol process wherein a residuum is subjected to a multi-stage, countercurrent liquid-liquid extraction process utilizing a relatively polar solvent, e.g., a mixture of cresylic acid and phenol, to extract aromatics, naphthenes and asphaltenes, and a relatively paraffinic solvent, e.g., propane, to extract paraffins, from the residuum.

The Duo-Sol process is utilized particularly in the manufacture of paraffinic lubricating oils containing a minimum of asphaltenes, as described, for example, in U.S. Pats. 1,912,349; 2,081,495; 2,070,385; 2,225,396 and 2,734,848. The process involves introducing a paraffinic solvent to a first stage in a countercurrent extraction system, a relatively polar solvent at a final stage and a residuum feed at an intermediate stage. A heavier extract fraction containing extracted asphaltenes is separated from the bottom of the feed stage and is transferred to one or more other stages between the residuum feed stage and the first stage, such stages being termed the Extract Section, for further extraction of paraffins. The extract fraction is withdrawn from the first stage, the polar solvent distilled therefrom and recycled for further use in the process. The remaining asphaltenes may then be subjected to downstream processing such as a cracking operation.

A lighter raffinate fraction containing extracted paraffins from the residuum is withdrawn from the top of the feed stage and transferred to one or more contacting stages between the feed stage and the final stage, such stages being termed the Raffinate Section, for further extraction of aromatics, naphthenes, and asphaltenes. The raffinate fraction flows out of the system at the final stage, the paraffinic solvent recovered and recycled and the paraffins from the residuum subjected to downstream processing such as dewaxing and distillation for further lubricating oil refinement.

Each of the aforementioned stages may be separate vessels, separate contacting regions in a horizontal chamber, or separate trays or packed column sections in a vertical extraction column. Such stages are well known in the art and are described in U.S. Pats. 2,054,245; 2,081,495; 2,081,497; 2,120,209; 2,131,422; 2,151,529; 2,201,550; 2,216,602; 2,400,378; and 2,647,856 and in Liquid Extraction, Treybal, First Edition, pp. 278–279.

It is conventional practice in the art to introduce the paraffinic solvent and the polar solvent at opposite ends of the extraction system and the residuum feed at an intermediate stage. Exceptions to the general and conventional practice are described in U.S. Pat. 2,225,396 wherein the paraffinic solvent is shown being introduced with the residuum feed as well as at the first stage, and in U.S. Pat. 2,754,247 wherein the residuum feed and a deasphalted residuum feed are shown being introduced at two separate intermediate stages. The ultilization of such unconventional type flow schemes are stated to increase considerably the capacity of the Duo-Sol plants. The processes, however, suffer certain disadvantages. In the process of Pat. No. 2,225,396, to be more fully discussed hereinafter, contact of the raw residuum feed with fresh propane precipitates asphaltenes in the feed stage and complicates phase separation therein and hence high asphaltic stocks cannot be advantageously processed. In the process of Pat. No. 2,754,247, an upstream deasphalting operation is required which increases the cost of the overall process.

Accordingly, the object of the invention is to improve the Duo-Sol process by providing a flow scheme which will increase the efficiency and/or capacity of the extraction process.

Another object of the invention is to increase the capacity of the Duo-Sol process wherein the flow conditions in or near the feed stage are close to flooding and/or wherein the feed contains a relatively high proportion of asphaltenes.

Other objects of the invention will be apparent from the following description of the invention.

STATEMENT OF THE INVENTION

The invention herein comprises introducing 5–50 volume percent, preferably 10–30 percent, of the total polar solvent into the intermediate residuum feed stage, preferably with the residuum feed to the intermediate stage. Another embodiment of the invention comprises introducing 1–5 percent, preferably 1–3 percent, of the total polar solvent with the paraffinic solvent to the first stage.

Another aspect of the invention consists in mixing, prior to introduction into the feed stage, the residuum feed and added polar solvent with the extract phase transferred from the Raffinate Section to the feed stage before contact with any raffinate transferred from the Extract Section to the feed stage. In this fashion, the feed is blended with a maximum of polar solvent and aromatics, naphthenes, etc., prior to contact with paraffins which precipitate asphaltenes.

It is believed that the efficiency of phase separation, particularly at the feed stage, is reduced by the presence of harmful asphaltene precipitates. In addition, the precipitated asphaltenes cause mechanical problems in pumps, heat exchangers and lines, etc. Contact of a raffinate containing a large proportion of paraffins with a raw residuum containing asphaltenes generally causes the asphaltenes to precipitate out into small particles. The problem is particularly acute when processing residua rich in asphaltenes, i.e., those having above 5 weight percent, preferably above 8 weight percent asphaltenes, as measured by the Pentane Precipitation Test to be defined hereinafter, and/or when

the flow conditions in and near the feed stage approximate flooding conditions, e.g., is 70 percent, preferably 85 percent of flooding, i.e., where a rapid decrease in efficiency results from a slight increase in flow. The problem is particularly acute at or near the feed stage wherein the feed contains a high asphaltene content so that the asphaltenes are particularly susceptible to precipitation.

The problem of asphaltene precipitation is believed overcome by insuring that the easily precipitated asphaltenes contact the polar solvent and are therefore diluted by and dissolved therein prior to, or at least simultaneously with, contacting a highly paraffinic stream such as raffinate from the Extract Section.

In any event, it has been found that the capacity and/or the efficiency of a Duo-Sol unit is substantially increased by introducing 5–50 percent, preferably 10–30 percent, of the polar solvent into the residuum feed stage. The remaining polar solvent is introduced at the final stage as is conventional in the art. The polar solvent is introduced into the residuum feed stage either directly or with the residuum, raffinate oil, or extract oil fed to the residuum feed stage. Preferably the polar solvent is admixed with the residuum prior to entry into the feed stage. In another embodiment, the efficiency of the first stage may be improved by introducing 1–5 percent, preferably 1–3 percent, of the polar solvent into the paraffinic solvent feed stage. It is also within the scope of the invention to introduce the polar solvent at both of the above points, i.e., into the rasiduum feed stage and into the paraffinic solvent feed stage. In that event, the amount of polar solvent introduced with the paraffinic solvent diminishes the amount introduced with the residuum feed, e.g., if 4 percent of the polar solvent is introduced with the paraffinic solvent, 5–46 percent is introduced with the residuum.

It is also within the scope of the invention to introduce a portion of the paraffinic solvent, e.g., propane, with the residuum feed as shown in U.S. Pat. 2,225,396 provided the paraffinic solvent is introduced into the feed downstream from the introduction of polar solvent in order to avoid the aforementioned asphaltene precipitation. In still another embodiment, the residuum feed, prior to entrance into the feed stage, is mixed with an extract phase (which contains the polar solvent) from the Raffinate Section prior to being mixed with a raffinate phase (which contains paraffins) from the Extract Section.

As previously discussed, it is believed that inadequate phase separation occurs due to the formation of asphaltene precipitates. The polar solvent blended with the residuum prior to the residuum contacting the high paraffinic raffinate, dissolves and/or dilutes the asphaltenes so that asphaltene precipitation is minimized. Prior to our invention, it was felt that introduction of the polar solvent at the feed stage might be detrimental in that it would decrease the amount of polar solvent utilized in the Raffinate Section to strip the raffinate of asphaltenes. Accordingly, it was quite surprising to discover that introduction of part of the polar solvent at the feed stage had a beneficial effect on the extraction and that it increased the capacity of the Duo-Sol unit.

DETAILED DESCRIPTION OF THE INVENTION

For purposes of the present disclosure, a paraffinic solvent is a solvent which has a selective solvency power for paraffins in a residuum feed. Suitable such solvents which are generally used include the C_2–C_{10} alkanes, e.g., ethane, propane, butane, and pentane, etc., a light paraffinic naphtha having a boiling range of about 500°–300° F. and the C_2–C_{10} alkanols, e.g., propanol, butanol, pentanol, hexanol, etc. Liquid propane is the most widely used paraffinic solvent in the Duo-Sol process and is preferred herein. The liquid propane may be mixed with lesser amounts of the lower paraffins such as ethane, butane, or pentane, but generally essentially pure liquefied propane is utilized.

The polar solvent may be any solvent having a selective solvency power for asphaltenes and suitable in a Duo-Sol process. Suitable polar solvents include liquid sulfur dioxide, cresol, cresylic acid, furfural, quinoline, pyridine, aniline, phenol, dichloroethyl ether, nitrobenzene, chloroaniline, benzol, etc. A preferred solvent is a mixture of cresylic acid and phenol, generally comprising 50–75, preferably 60–70 weight percent cresylic acid and 25–50, preferably 30–40 weight percent phenol, known in the art as Selecto. Cresylic acid and phenol alone, however, are suitable, phenol being preferred due to its relative inexpensiveness.

The Duo-Sol feed may be any topped crude oil, heavy petroleum fraction, heavy crude or any mineral oil which is generally subjected to an extraction treatment to separate paraffins or a lubricating oil fraction from aromatics, naphthenes and/or asphaltenes. For purposes of discussion, the feed is referred to herein as residuum. As stated hereinabove, the invention is most useful when the feed contains a relatively large proportion of asphaltenes, e.g., above 5 weight percent, preferably above 8 weight percent asphaltenes as determined by the Pentane Precipitation Test, generally described in American Petroleum Institute Proceedings, 14th Annual Meeting, Chicago, Ill., October 23–26, 1933, pages 96 et seq. The residuum is treated with about ten times its volume of n-pentane at 80° F. and the amount of precipitated asphaltenes weighed. As indicated in the above-cited publication, the amount of asphaltenes precipitated by propane is about 5 times that using pentane, and so the above-stated minimum asphaltenes contents are lower than if a propane standard were utilized. The invention is also particularly useful where the residuum feed contains a relatively high amount of saturates, and/or mono- and di-aromatics, e.g., over 38 weight percent saturates, over 11 percent mono-aromatics, and over 12 percent di-aromatics as does the residuum derived from 33°–40° API Alaska crude oil.

The detailed process flows are the same as in known Duo-Sol processes except for the split introduction of the polar solvent and the other process variations generally described above. The figure is a schematic flow diagram of the extraction system of the invention in a Duo-Sol process, it being understood that the necessary mechanical equipment such as pumps, exchangers, etc., and auxiliary apparatus known in the art are omitted for purposes of simplification, and that the extraction stages may be separate vessels, chambers or trays in an extraction column, etc., the particular type of stages not being of the essence of the invention. Seven stages are shown, however, the number of stages is not critical to the invention and may encompass a fewer or a greater number of stages, such as the nine stages shown in the aforementioned patents. Stages **1** and **2** are labelled the Extract Section since in that section the oil contains a higher proportion of the extract and undesired asphaltenes, aromatics and asphaltenes than in the Raffinate Section. Stage **3** is designated the Feed Section. Stages **4**–**7** are designated the Raffinate Section in that the processed oil contains a higher proportion of paraffins.

The residuum feed is fed via line **1** into feed stage **3**. The polar solvent, shown for illustration as Selecto, is preferably introduced via line **2** into the residuum feed prior to its combined entrance into the feed stage. A conventional in-line mixer may be utilized to blend the Selecto with the residuum feed. The Selecto may be introduced into the feed stage or with the raffinate or extract fed to the feed stage, however, it is preferred that the Selecto be blended with the residuum prior to their combined entrance into the feed stage. In the embodiment where a paraffinic solvent, shown as propane for purposes of illustration, is blended with the residuum feed as described in U.S. Pat. 2,225,396, the paraffinic solvent is preferably added downstream of the point where the Selecto is injected into the residuum stream to minimize asphaltene precipitation, and is shown

herein as introduced via line 3 into the mixed residuum-Selecto stream.

The bulk of the paraffinic solvent is introduced via line 4 into stage 1. In one embodiment of the invention, Selecto is also introduced, via line 5, with the liquid propane prior to their combined entrance into stage 1.

The balance of the Selecto not introduced into the feed stage is introduced via line 6 into the final stage 7. The Selecto flows countercurently to the raffinate phase in the multi-stage vessel or column and is withdrawn via line 7 as an extract phase containing the dissolved asphaltenes, naphthenes and aromatics. The liquid propane entering the system via line 4 into stage 1 flows countercurrently to the extract phase and is withdrawn via line 8 from stage 7 in a raffinate phase containing the dissolved paraffins.

Referring now to the feed stage 3, the residuum with the added Selecto preferably, but not necessarily, first contacts an extract phase transferred from stage 4 via line 9, and then a raffinate phase transferred from stage 2 via line 10 and enters the feed stage 3. Any propane introduced with the feed is preferably introduced downstream of the point of entrance of the aforementioned phases. In stage 3, a heavier extract phase is separated from a lighter raffinate phase. The extract fraction is withdrawn via line 12 and transferred to stage 2 in the Extract Section. In stage 2 the extract phase contacts a raffinate fraction from stage 1 which strips paraffins from the extract phase. A less paraffinic extract phase is withdrawn from stage 2 via line 13 and transferred to stage 1 where it contacts the liquid propane. Additional paraffins are extracted in stage 1 from the extract phase by the liquid propane and the extract phase containing the asphaltenes, aromatics and naphthenes as well as Selecto is withdrawn from the extract system via line 7. The extract phase is then subjected to distillation and/or other known processing wherein aromatics, naphthenes and asphaltenes are separated from the Selecto solvent which is recycled for reuse in the abovedescribed process. A raffinate phase from stage 1 is transferred via line 14 into stage 2 where it conducts an extract phase and is transferred via line 10 into stage 3 or, in the preferred embodiment into the residuum, prior to introduction into the feed stage.

The raffinate extracts paraffins from the residuum in stage 3 and is withdrawn overhead via line 15 and transferred to stage 4 of the Raffinate Section. In stage 4 the raffinate is mixed with extract from stage 5 and aromatics, naphthenes, and asphaltenes are removed from the raffinate by the extract phase. The extract is taken from the bottom of stage 4, via line 9 and transferred to stage 3 or, in the preferred embodiment, mixed with the incoming residuum feed after introduction of Selecto. The raffinate extracts paraffins from the extract phase in stage 4, is removed overhead via line 16 and transferred to stage 5. In similar fashion the raffinate extracts paraffins from the extract in stage 5 with a raffinate phase taken overhead via line 18 and transferred to stage 6 and an extract phase removed via line 17 and transferred to stage 4. The raffinate from stage 6 is transferred via line 20 into the final stage 7 where it contacts Selecto which further extracts aromatics, asphaltenes and naphthenes. The raffinate which contains the desired paraffins is taken overhead from final stage 7 via line 8, then subjected to distillation and/or other known processing to remove propane from the product paraffins, and the propane is recycled for further use in the process.

The aforementioned process and the improved results therefrom will be illustrated by, and apparent from, the following examples:

Example 1

A Duo-Sol unit containing seven (7) stages utilizing propane as the paraffinic solvent and Selecto (90% phenol-10% cresol) as the polar solvent was operated in conventional manner, i.e., propane introduced at stage 1, residuum at stage 3 and all the Selecto at stage 7. The feed was a residuum derived from Alaskan crude, had a viscosity of 199 S.S.U. and contained about 8.3 weight percent asphaltenes as determined by n-pentane precipitation. The residuum contained about 39.0 weight percent saturates, 12.3 percent monocyclic aromatics, 13.6 percent dicyclic aromatics, 9.3 percent polycyclic aromatics, 25.6 heterocyclic nitrogen and oxygen aromatics, and 0.2 percent sulfides. The residuum feed rate was 8,600 barrels per day, the propane feed rate was 38,350 barrels per day, and the Selecto feed rate was 23,500 barrels per day. The yield of raffinate oil, propane excluded, was 4,650 barrels per day. When the residuum feed rate was increased to 8,800 barrels per day, and the propane and Selecto rates increased proportionately, poor separation occurred at the feed stage and extract accumulated in the adjacent Raffinate Section stages with consequent operational instability.

About 5,000 barrels per day of Selecto was then introduced into the feed stage with the amount of Selecto to stage 7 reduced by a like amount to about 18,500 barrels per day. The residuum feed rate was increased to 10,000 barrels per day, the propane feed rate was increased to 40,600 barrels per day and the total Selecto feed rate was increased to 28,700 barrels per day (5,000 barrels per day to stage 3, balance to stage 7). The raffinate oil yield increased to 5,100 barrels per day and the operation was stable. Further increases were not attempted due to reasons other than limitations in unit capacity.

Example 2

The above comparative experiment was repeated with the residuum feed comprising 10,700 barrels per day of a blend of 22 volume percent San Joaquin residuum and 78 percent of the aforedescribed Alaskan residuum, the blend containing 7.4 weight percent asphaltenes. The San Joaquin residuum contained about 36.9 weight percent saturates, 9.9 percent monocyclic aromatics, 9.1 dicyclic aromatics, 12.3 polycyclic aromatics, 30.9 percent heterocyclic nitrogen and oxygen aromatics and 0.9 percent sulfides. The propane feed rate was 42,400 barrels per day and the total Selecto feed rate was 28,600 barrels per day. The operation was highly unstable with extract accumulating in stage 4 and there was poor phase separation in the feed stage and in stage 1.

About 5,500 barrels per day of Selecto was diverted from stage 7 to the feed stage. The operation stabilized, phase separation improved and the raffinate oil, propane excluded, was continuously produced at 5,300 barrels per day. Further increases in residuum feed were not attempted due to mechanical limitations.

We claim:

1. In a Duo-Sol extraction process wherein an asphaltic crude oil residuum is subjected to multi-stage countercurrent liquid-liquid extraction utilizing a paraffinic solvent introduced at a first stage to extract paraffins and a polar solvent introduced at a final stage to extract aromatics, naphthenes and asphaltenes, and wherein the residuum is introduced at a stage intermediate to said first and final stages, the improvement of introducing 5–50 volume percent of the polar solvent into said intermediate residuum feed stage and introducing the remainder of said polar solvent to said final stage, or to said final stage and said first paraffinic solvent feed stage.

2. The method of claim 1 wherein said 5–50 volume percent of polar solvent is introduced with the residuum fed to said intermediate feed stage.

3. The method of claim 2 wherein 10–30 volume percent of said polar solvent is introduced with said residuum.

4. The method of claim 1 wherein 1–5 percent of the polar solvent is introduced into said first paraffinic solvent feed stage.

5. The method of claim 1 wherein said paraffin solvent is propane and said polar solvent is selected from the

group consisting of cresylic acid and phenol and mixtures thereof.

6. The method of claim 1 wherein said residuum contains over 5 weight percent asphaltenes as determined by pentane precipitation.

7. The method of claim 5 wherein the flow rate in the feed stage is above 70 percent of flooding.

8. The method of claim 6 wherein said residuum contains over 8 weight percent asphaltenes and wherein said flow rate is above 85 percent of flooding.

9. The method of claim 1 wherein all of said remainder of polar solvent is introduced to said final stage.

References Cited

UNITED STATES PATENTS

2,754,247	7/1956	Fast et al.	208—317
3,414,506	12/1968	Campagne	208—309
2,225,396	12/1940	Anderson	208—317

HERBERT LEVINE, Primary Examiner

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