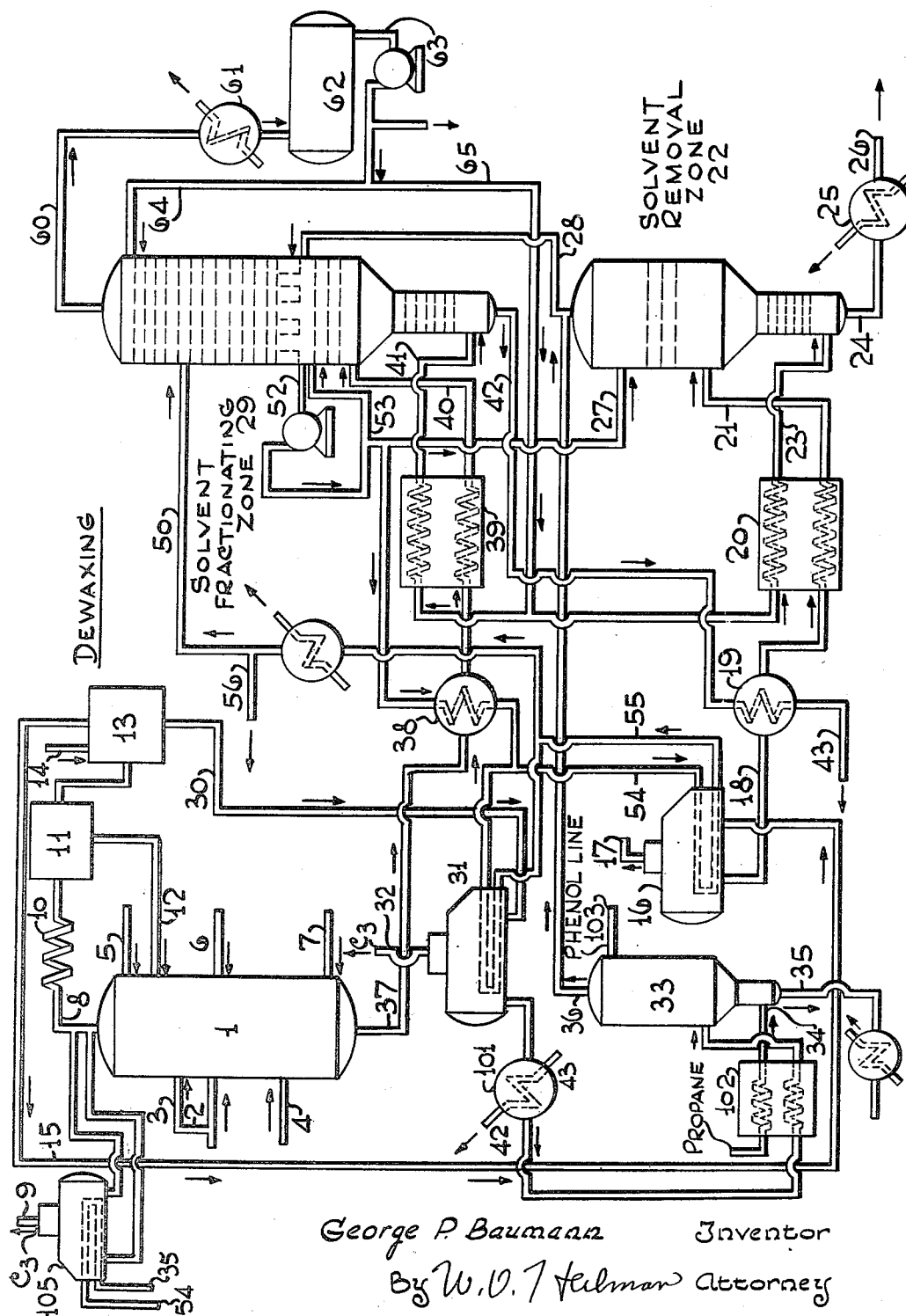


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G. P. BAUMANN
COMBINATION DEASPHALTING, PHENOL
TREATING, AND DEWAXING PROCESS
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COMBINATION DEASPHALTING, PHENOL
TREATING, AND DEWAXING PROCESSGeorge P. Baumann, Metuchen, N. J., assignor to
Standard Oil Development Company, a corpo-
ration of Delaware

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The present invention is concerned with an improved deasphalting, phenol treating and dewaxing process, and relates more particularly to the recovery of the solvents utilized in these operations.

The invention is especially concerned with an improved lubricating oil operation wherein the processing steps of deasphalting, dewaxing and phenol treating are combined. In accordance with the specific adaptation of the present invention, a distillate feed stream from a conventional vacuum flasher as well as a residuum from the vacuum flasher are separately introduced into a combination treater tower. The residuum is countercurrently treated with propane or an equivalent deasphalting solvent in the lower portion of the tower for deasphalting. The deasphalted stream passes up the tower being partially treated with phenol or an equivalent solvent before combining with the distillate feed for final quality improvement. The raffinate mixture containing phenol as well as propane passes directly to a conventional dewaxing plant. The effluent wax mixture from the dewaxing plant combines with the extract-asphalt solution before solvent recovery. The dewaxed oil mixture is separately processed for dewaxed oil recovery. The solvent recovery from this stream is partially integrated, in a novel fashion, with the solvent recovery from the extract-asphalt-wax solution. Propane is used for stripping phenol from the flashed oil stream.

It is well known in the art to treat feed oils, particularly distillate feed oils, with various solvents in order to separate the relatively more aromatic type constituents from the relatively more paraffinic type constituents. Solvents generally employed are phenol, various cresols, sulfur dioxide and the like. In these operations the feed oil is usually contacted with the selected solvent such as phenol either in a countercurrent treating operation or in a multi-stage batch operation under temperature and pressure conditions to secure phase separation. As a matter of practice, the oil to be treated is usually introduced into one end of a countercurrent treating zone while the solvent or solvent mixture is introduced at the other end. The solvent and oil flow countercurrently under temperature and pressure conditions whereby phase separation is secured. The solvent rich or solvent extract phase is withdrawn from one end of the countercurrent treating zone, while the solvent poor or the raffinate phase, comprising the more paraffinic type constituents, is withdrawn from the

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other end of the treating zone. The respective streams are then handled in a manner to segregate the solvent from the oil.

It is also known in the art to conduct a light hydrocarbon deasphalting process. In a process of this character, an oil phase or feed stream containing asphaltic type constituents is mixed with a light hydrocarbon solvent such as, for example, liquid propane under temperature and pressure conditions whereby the asphaltic type constituents are thrown out of solution. After separation of the asphaltic type constituents from the deasphalted oil, the respective streams are handled in a manner to recover the solvent.

It is also known in the art to remove waxy constituents from a paraffinic type oil containing the same in order to improve the quality of the oil. This is usually accomplished by employing a dewaxing solvent such as propane, methyl ethyl ketone or a similar dewaxing solvent. In operations of this type, the waxy oil and the solvent are usually heated to a temperature to secure a single phase or substantially complete miscibility of the ingredients. The waxy mixture is then chilled in order to precipitate wax particles or crystals from the solution. The chilled mass is filtered in order to segregate the wax particles and further handled in a manner to recover the dewaxing solvent, and to further refine the dewaxed oil and the segregated waxes.

It has now been discovered that an improved combination process may be employed providing the respective feed streams are handled in a particular manner, especially with respect to the recovery of the solvents from these streams.

The present invention may be readily understood by reference to the drawings illustrating one embodiment of the same.

Referring specifically to the figure, a distillate hydrocarbon feed is introduced into about the middle section of a combination treater zone 1 by means of line 2. If desired, and under certain conditions, it may be desirable to introduce the feed at a point between the middle third and upper third of zone 1 by means of line 3.

A residuum hydrocarbon feed is introduced into zone 1 by means of line 4 at a point between about the middle third and the lower third of the combination treater zone.

In accordance with the present invention, a solvent having a preferential selectivity for the more aromatic type constituents, as, for example, phenol, furfural, nitrobenzene, various organic nitrates, acetates and other esters, and the like, is introduced into the top of zone 1 by means

of line 5. These so-called polar solvents may be used in admixture or modified by various modifying solvents such as water and the like. The preferred solvent comprises phenol. Also in accordance with the present invention, it is preferred to introduce a portion of the phenol or equivalent solvent into approximately the middle of zone 1 by means of line 6.

A light hydrocarbon deasphalting solvent, as, for example, a liquefied normally gaseous hydrocarbon such as propane, is introduced into the bottom of zone 1 by means of line 7. Under the conditions of operation a raffinate phase comprising paraffinic type constituents, a relatively large quantity of propane and a small amount of phenol or equivalent solvent is removed overhead from zone 1 by means of line 8. This stream, if desired, may be subjected to a simple flash in order to remove excess propane by means of line 9, not required in the initial dewaxing step. In accordance with a preferred adaptation of the present invention, the stream is passed through a cooling zone 10 into a separation zone 11 wherein phase separation occurs. The solvent-rich phase is withdrawn from separation zone 11 by means of line 12 and re-introduced into the top of zone 1 below the point of the introduction of the phenol stream which is introduced into zone 1 by means of line 5. The oil-rich phase is removed from separation zone 11 and introduced into a dewaxing zone 13.

Additional propane may be introduced into dewaxing zone 13 by means of line 14. This will be necessary providing autorefrigeration is employed in zone 13 in order to make up for the propane or equivalent solvent evaporated. The dewaxing zone may comprise any suitable number and arrangement of stages.

The dewaxed oil solution is removed from zone 13 by means of line 15 and passed to dewaxed oil solvent recovery facilities in order to remove and recover the solvent from the dewaxed oil.

The dewaxed oil solution is introduced into propane recovery zone 16 which is maintained under temperature and pressure conditions adapted to remove overhead by means of line 17 a substantial amount of the propane. The dewaxed oil solution is withdrawn from zone 16 by means of line 18, passed through heating exchanging medium 19, and then passed through heating zone 20 wherein the temperature is brought to the desired degree. The heated dewaxed oil stream is withdrawn from zone 20 by means of line 21 and introduced into a solvent removal zone 22 which is maintained under temperature and pressure conditions adapted to substantially completely free the dewaxed oil of solvent. The oil flows downwardly in zone 22 countercurrently contacting upflowing stripping propane which is introduced into the bottom of zone 22 by means of line 23. A dewaxed oil free of solvent is removed from zone 22 by means of line 24, passed through a cooling zone 25 and withdrawn from the system by means of line 26.

Phenol is introduced into the top of zone 22 by means of line 27 in order to remove any distilled oil constituents from the upflowing vapors. A solvent mixture comprising phenol and propane is removed overhead from zone 22 by means of line 28 and introduced into a solvent fractionating zone 29.

The waxy solution segregated in zone 13 is removed by means of line 30 and passed to wax solvent recovery facilities. This stream is introduced into zone 31 which is maintained under

temperature and pressure conditions adapted to remove overhead by means of line 32 a substantial amount of the propane. The waxy mixture is then passed through heat exchanging medium 101 and then passed through heating zone 102 wherein the temperature is brought to the desired degree. The heated wax stream is introduced into zone 33 by means of line 34 wherein temperature and pressure conditions are adapted to substantially completely free the wax of solvent. Stripping propane is introduced into zone 33 by means of line 34, while the wax constituents free of solvent are removed from zone 33 by means of line 35 and further handled and defined as desired.

Phenol is introduced into the top of zone 33 by line 103 in order to remove any distilled oil constituents from the upflowing vapors. The phenol propane mixture removed from the wax is taken overhead from zone 33 by means of line 36 and introduced into zone 29.

A solvent extract phase comprising asphaltic constituents is removed from the bottom of zone 1 by means of line 37 and passed into solvent recovery facilities. This stream is passed through a heat exchanging zone 38 and then through furnace 39 wherein the temperature is raised to the desired level. This stream is introduced into solvent fractionating zone by means of line 40 wherein temperature and pressure conditions are adjusted to remove the solvent from the asphaltic constituents. These asphaltic constituents flow downwardly in zone 29 and are stripped of solvent by means of propane which is introduced by means of line 41. The asphaltic constituents are removed from the bottom of zone 29 by means of line 42, passed through heat exchange zone 19 and 101 and then removed from the system by means of line 43. If it is desired to combine the wax and the asphaltic constituents, a preferred method of operation is to combine the waxy solution of line 30 with the solvent extract solution of line 37 and process these streams simultaneously. Under these conditions, the stream removed by means of line 43 comprises asphaltic constituents and wax and equipment 31, 101, 102 and 33 and attendant facilities and lines may be deleted.

Propane and phenol vapors pass upwardly in zone 29 and countercurrently contact phenol which is introduced into the upper area by means of line 50. Phenol condenses in a collecting zone 51 and zone 29, is removed by means of line 52 and a portion of the same re-introduced into the zone 29 by means of line 53. A portion of the phenol is introduced into the top of zones 22 and 33 by means of lines 27 and 103, as illustrated. The remaining phenol passes through heat exchangers 38 and is then introduced as a heat exchange medium into zones 16, 31 and 105 by means of line 54. This phenol is withdrawn by means of line 55 and passed to storage by means of line 56. Normally, this phenol is reintroduced into zone 1 by means of lines 5 and 6, as illustrated.

Propane is removed overhead from zone 29 by means of line 60, condensed in cooling zone 61 and passed to a separator 62. Liquid propane is withdrawn from zone 62 by means of line 63 and passed to storage where it can be re-introduced into zone 1 by means of line 7. A portion of the propane is introduced into the top of zone 29 by means of line 64 while another portion is segregated by means of line 65 and used as a stripping gas in zones 29, 33 and 22. This pro-

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pane is introduced into these zones by means of lines 41, 34 and 23 respectively.

The invention is broadly concerned with an improved method for refining petroleum oils boiling in the lubricating oil boiling range. In accordance with the present invention, a crude oil is processed through a vacuum flasher zone rather than through a conventional pipe-still or equivalent means wherein a sharp separation is secured. Normally it is preferred to process in the vacuum flasher 20 to 40% of the highest boiling crude bottoms. For example, if 35% crude bottoms (atmospheric pressure) is processed, this stream is heated to a temperature in the range of 750 to 800° F. and then flashed in the vacuum flasher at a pressure in the range of 50 to 200, preferably at about 100 millimeters absolute pressure. Under these conditions, a distillate fraction boiling in the range of about 600 to 1100° F. is segregated from a residuum fraction boiling above about 900° F.

The two said streams from the vacuum flasher are separately introduced into the combination treater tower. The residuum is countercurrently treated with propane or an equivalent solvent in the lower portion of the tower for deasphalting. The bright stock passes up the tower being partially phenol treated before combining with the distillate feed for final quality improvement.

In accordance with the present invention vacuum residuum and wide-cut lube distillate feed stocks are pumped into a combination propane deasphalting and phenol treating tower. The residuum is separately introduced in the lower portion of the tower being countercurrently contacted with propane for deasphalting. The raffinate from the residuum, i. e., bright stock, passes upward, countercurrent to a phenol bearing distillate extract from the upper portion of the tower. The bright stock is thereby partially phenol treated subsequent to deasphalting. The quality-improved bright stock then passes into the distillate-phenol treating portion of the tower where it combines with distillate to be further countercurrently treated with phenol. The extract from the tower contains most of the phenol in solution with propane, propane rejected asphalt, and the low-quality phenol extracted oil. The raffinate contains most of the propane with quality-improved oil in solution with soluble phenol.

The raffinate solution is sent directly to a propane dewaxing plant. The phenol in the raffinate acts as a wax diluent or solvent, the majority of it passing out of the system in the wax mixture from the filters.

For the operations of deasphalting, dewaxing, and phenol treating, only three solvent-bearing streams must be processed in recovery equipment. These are the dewaxed oil mixture, the wax mixture, and the asphalt-extract mixture. If wax is not required as a separate product, the wax mixture and the asphalt-extract mixture are combined for solvent recovery.

The temperatures and pressures utilized in the combination treater zone may vary appreciably depending upon the characteristics of the respective streams being processed. In general, it is preferred that the temperatures be in the range of about 50° F. to 200° F. and pressures in the range of 100 to 500 lbs. per square inch gauge be utilized. A satisfactory temperature is about 120° F. while a satisfactory pressure is about 250 lbs. per square inch gauge.

Although phenol is preferred as the solvent,

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other equivalent solvents may be utilized. In general the solvent should be selected from that class of solvents having a preferential selectivity for the relatively more aromatic type constituents as compared to the relatively more paraffinic type constituents. Mixtures of these solvents as well as solvent modifying agents such as water and the like may be utilized. In general the amount of phenol introduced into the top of the treater may range from about .5 to 5 volumes of phenol per volume of oil. A desirable solvent to oil ratio is in the range of about 1:1. The amount of phenol introduced in the center of the treater likewise may vary appreciably. In general it should be approximately half the amount introduced at the top of the zone.

Any suitable deasphalting solvent may be used other than propane although propane or a solvent comprising propane is desirable. The quantity of propane utilized based on the quantity of total feed is from 3 to 15 volumes of propane per volume of feed. A satisfactory amount is about 6 volumes of propane per volume of feed.

The raffinate stream removed overhead from zone 1 will vary appreciably in composition, generally having a relatively large amount of propane present. Under suitable conditions of operation this raffinate stream may comprise about one volume of oil, ½ volume of phenol and about 5 volumes of propane. In accordance with the preferred embodiment of the invention, this stream is cooled to about 90° F. in order to secure the separation of a phenol rich phase which is returned to zone 1 as described. The oil phase is passed to a dewaxing zone wherein the same is cooled at a predetermined rate in order to precipitate wax crystals. These crystals are removed from the oil preferably by filtering or other equivalent means. Generally, the waxy oil is cooled to a temperature in the range of 20° F. to -50° F. or lower in order to secure satisfactory precipitation of the wax crystals.

The extract solution removed from the bottom of the treating zone will also vary appreciably in composition. A typical composition of this stream comprises one volume of oil, about 2 volumes of phenol and about 2 volumes of propane.

As described, the solvent recovery facilities for the dewaxed oil, the wax solution and the solvent extract solution are interrelated in a manner to secure improved solvent recovery.

The dewaxed oil solution rich in propane and containing a relatively small amount of phenol is processed by passing the same through a zone adapted to remove a large amount of the propane and then passing the stream to a zone wherein the final traces of solvent are removed. The solvent stream overhead from this latter zone comprises phenol and propane which mixture is handled in the extract solution zone in order to segregate the respective solvents.

In handling the dewaxed oil solution, a temperature of about 150° F. ranging from 125 to 175° F. is employed in the initial solvent recovery zone. This stream is then introduced into an intermediate point of the solvent removal zone at a temperature of about 600° F. The temperature at the bottom of this zone is in the range from about 540 to 580° F., preferably about 560° F.

The temperature maintained at the bottom of the solvent fractionating zone is in the range of about 550° F. to 650° F., preferably at about 600° F. The temperature maintained in the phenol recovery section of zone 29 is in the range from

about 500° F. to 550° F., preferably about 520° F.

Thus, the present invention comprises a simplified lube plant combining the deasphalting, the dewaxing and the solvent treating stages. Vacuum residuum and wide-cut lube distillate feed stocks are pumped into a combination propane deasphalting and phenol treating tower. The residuum is separately introduced in the lower portion of the tower being countercurrently contacted with propane for deasphalting. The raffinate from the residuum, i. e., brightstock, passes upward, countercurrent to a phenol bearing distillate extract from the upper portion of the tower. The brightstock is thereby partially phenol treated subsequent to deasphalting. The quality-improved brightstock then passes into the distillate-phenol treating portion of the tower where it combines with distillate to be further countercurrently treated with phenol. The extract from the tower contains most of the phenol in solution with propane, propane rejected asphalt, and the low-quality phenol extracted oil. The raffinate contains most of the propane with quality-improved oil in solution with soluble phenol.

The raffinate solution is sent directly to a propane dewaxing plant. The phenol in the raffinate acts as a wax diluent or solvent, the majority of it passing out of the system in the wax mixture from the filters.

For the operations of deasphalting, dewaxing, and phenol treating, only three solvent-bearing streams must be processed in recovery equipment. These are the dewaxed oil mixture, the wax mixture, and the asphalt-extract mixture. If wax is not required as a separate product, the wax mixture and the asphalt-extract mixture are combined for solvent recovery.

A distinct improvement is secured by the method of handling the various solvent recovery streams. The extract-asphalt and wax mixture is preheated and flashed into a fractionating tower. The tower is operated at a pressure sufficiently high to permit condensing the overhead propane with cooling water. The fuel oil quality bottoms is stripped of phenol with superheated propane. A phenol sidestream containing 2 to 4% propane is withdrawn. Complete separation of the two solvents is not attempted since pure solvents are not required in the treating step.

The dewaxed oil, containing a relatively high mol percentage of propane, is pre-flashed in a kettle-type reboiler. Propane vapors are taken off and combined with the overhead from the extract tower. The liquid from the propane vaporizer is further preheated and injected into the dewaxed oil flash tower operating at the same pressure. The raffinate oil is phenol-stripped with superheated propane. The phenol and propane vapors from the dewaxed oil flash tower are introduced in the extract tower below the phenol-side-stream pumparound pan. Thus, the propane and phenol recovery from both solvent-bearing streams is integrated, with corresponding equipment reduction and simplification.

The propane reflux drums serve the dual purpose of work drums and storage drums. A pressure-phenol work tank is provided for operation in conjunction with a normal atmospheric storage tank. A small phenolic water absorber is provided to recover the settled phenol from the overhead propane reflux drums. Although no steam stripping is employed, the absorber is installed to remove water from the unit which enters with the oil feed, or during a turnaround.

The wide-cut dewaxed oil is pressurized to intermediate tankage and the extract-wax-asphalt mixture passes to refinery fuel. The wide-cut dewaxed oil is separated into the desired lube base stocks by vacuum distillation, cutting to about 20% brightstock bottoms. The vacuum distillation is the final finishing step for the distillates. The bottoms is separately fed to a small clay contacting unit for finishing the brightstocks.

This invention covers the process and apparatus for a simplified solvent recovery system wherein the solvents employed in the treating step are a relatively high boiling solvent and a low boiling solvent; for example, phenol and propane respectively. Water may or may not be present. The invention comprises the integration of the solvent recovery systems by separating the majority of both solvents from the oil by distillation, and the use of the low boiling solvent for stripping the oil for complete removal of the solvents. This results in appreciable reduction in the number of pieces of equipment involved in solvent removal. The form of the integration in the combination deasphalting phenol treating and dewaxing unit is as follows:

When the wax solvent stream from the dewaxing step is combined in the extract solvent mixture, only two recovery systems are required. Consider the extract solvent mixture in which the propane phenol ratio is about 1:1. The mixture is preheated in heat exchange and heated further in a fired coil to about 640° F. The mixture is flashed into a tower operating at about 200 p. s. i. g. This pressure is necessary in order to condense propane with cooling water. A majority of the solvents, propane and phenol, and some oil are vaporized and rise in the tower. Pumpback phenol reflux is employed to condense the oil and prevent it from being taken off with the phenol. The oil plus some solvent, principally phenol, is stripped of the solvent by superheated propane vapors. The oil is solvent free and is sent to storage or to further processing.

The propane and phenol vapors pass up the tower and phenol with a small amount of propane is withdrawn as a side stream after condensation by means of a pumparound reflux stream. Propane and water, if present, are taken overhead and condensed for top reflux and liquid product. Water is separated by settling. The use of propane as one of the two solvents permits its use as a stripping medium. However, steam may be employed but it requires the subsequent separation of phenol and water.

The dewaxed oil solvent mixture in which the propane phenol ratio is about 16:1 may be handled in the same manner. However, for economic heat utilization, a majority of the propane is vaporized at low temperature and 200 p. s. i. g. in a simple kettle type reboiler. The propane is condensed with the propane from the extract tower. The dewaxed oil plus solvent is then heated by exchange and a fired coil to about 550-600° F. in order to vaporize most of the remaining solvents. The oil carried overhead is condensed by phenol reflux and combined with a liquid portion of the flash vaporization and is stripped of solvents with superheated propane vapors. The overhead solvent vapors may be handled as explained above in the extract solvent stream, or they may be fed below the pump-around system of the extract recovery tower for separation of phenol and propane.

In this process, complete separation of the two solvents is not made since it is not required

in the treating step. However, if pure solvents were required, the oil-free solvent vapors resulting from the flash and stripping operations may be partially condensed for heat recovery and combined as feed to a solvent tower for complete separation. In this case, another tower, fired coil, and attendant facilities will be necessary.

Having described the invention, it is claimed:

1. Process for the production of a high quality lubricating oil from a wax bearing distillate hydrocarbon oil and a residuum oil containing asphaltic constituents which comprises introducing the distillate oil into the center area of an extraction-treater zone, introducing the residuum oil into the extraction-treater zone below the point of introduction of the distillate oil, introducing a solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type constituents into the upper area of said extraction-treater zone, introducing a deasphalting solvent into said extraction-treater zone below the point of introduction of said residuum oil, withdrawing a solvent extract phase from the bottom of said extraction-treater zone, withdrawing a raffinate phase comprising paraffinic type constituents from the top of said extraction treater zone and handling said raffinate phase to separate a lubricating oil phase and a waxy phase, introducing said solvent extract phase into a solvent fractionating zone, removing a solvent free extract phase from the bottom of said solvent fractionating zone, removing the solvent having a preferential selectivity for aromatic type constituents from an intermediate point of said solvent fractionating zone and removing said deasphalting solvent from the top of said solvent fractionating zone and introducing a portion of said deasphalting solvent into the lower section of a secondary solvent removal zone, introducing said lubricating oil phase into an initial solvent separation zone wherein the majority of said deasphalting solvent is separated therefrom, withdrawing said lubricating oil phase from said initial solvent separation zone and introducing the same into said secondary solvent removal zone at a point above the point of introduction of said deasphalting solvent, wherein said lubricating oil phase is treated in a manner to remove the remainder of said deasphalting solvent and all of said solvent having a preferential selectivity for aromatic type constituents as a solvent mixture, passing said solvent mixture into said solvent fractionating zone and segregating the respective solvents from each other.

2. Process as defined by claim 1, wherein said waxy phase is combined with said solvent extract phase before introducing the same into said solvent fractionating zone.

3. Process as defined by claim 1 wherein a portion of the solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type constituents is introduced into said extraction-treater zone at a point between the point of introduction of said distillate oil and said residuum oil.

4. Process as defined by claim 1 wherein said solvent having a preferential selectivity for said aromatic type constituents as compared to paraffinic type constituents comprises phenol and wherein said deasphalting solvent comprises liquefied propane.

5. Process as defined by claim 1 wherein said raffinate phase withdrawn from the top of said extraction-treater zone is treated with said propane in a manner to remove waxy constituents therefrom.

6. Process as defined by claim 1 wherein said distillate hydrocarbon oil and said residuum oil are secured by vacuum flashing a crude oil in a manner to segregate a distillate oil and a residuum oil.

7. Process as defined by claim 1 wherein said distillate oil boils in the range from about 600° F. to 1100° F. and wherein said residuum oil boils above about 900° F.

8. Process as defined by claim 1 wherein said raffinate phase withdrawn overhead from said extraction-treater zone is cooled whereby a solvent rich phase separates, reintroducing said solvent rich phase into said extraction-treater zone at a point below the point of introduction of said solvent having a preferential selectivity for the relatively more aromatic type constituents as compared to the relatively more paraffinic type constituents.

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