

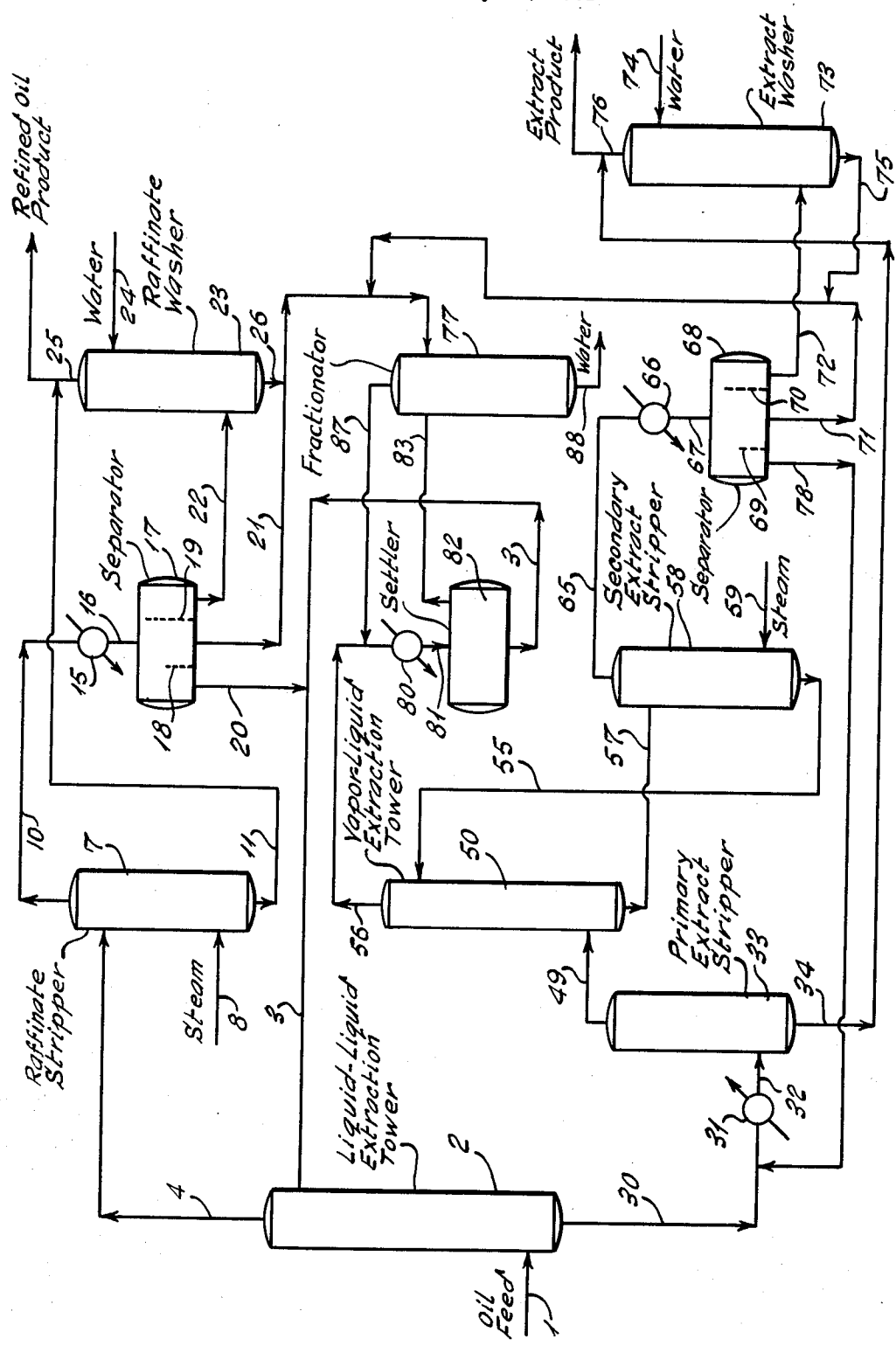
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HYDROCARBON TREATMENT PROCESS

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## HYDROCARBON TREATMENT PROCESS

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This invention is directed to a hydrocarbon treatment process employing liquid-liquid solvent extraction. More particularly, it relates to a method of solvent refining hydrocarbons containing a small portion of constituents co-boiling with the solvent. In accordance with the process of this invention, hydrocarbon oils containing constituents co-boiling with the solvent are contacted with a solvent in a liquid-liquid extraction zone forming separate primary extract and raffinate phases. The primary extract phase or a portion thereof is vaporized and contacted with a relatively high boiling hydrocarbon oil under vapor-liquid solvent extraction conditions effecting separation of solvent vapor free of co-boiling hydrocarbons from a secondary extract comprising said co-boiling hydrocarbon oil in solution with said relatively high boiling hydrocarbon oil. Said solvent vapor, free of co-boiling hydrocarbon oil, is condensed forming a purified solvent stream for recycle to said liquid-liquid extraction step.

In solvent refining processes wherein the solvent and material treated have substantially different boiling ranges, the solvent is readily separated from the extract and raffinate phases by simple distillation. However, separation by simple distillation is incomplete when the oil treated contains components having true boiling points in the region of the boiling point or boiling range of the solvent. For example, hydrocarbon oils having initial boiling points by ASTM distillation of less than about 625° F. may contain some components having true boiling points as low as about 325° F. Therefore, in treating hydrocarbon oils having initial boiling points by ASTM distillation less than about 625° F. with furfural as a solvent, oils co-boiling with the furfural tend to accumulate in the solvent thereby reducing its solvent power and its selectivity for extraction. Heretofore, it has been proposed that these co-boiling hydrocarbons be separated from solvents by azeotropic distillation wherein a low boiling azeotrope of solvent and water is distilled from the hydrocarbon. However, although azeotropic distillation is effected at a temperature substantially below the temperature of the boiling point of the pure solvent, substantial amounts of low boiling hydrocarbons may be vaporized with the azeotrope particularly when treating relatively low boiling stocks such as kerosene, diesel fuel, and hydraulic oils. In another prior art solution to this problem, the extracted oil is re-extracted from the solvent by liquid-liquid extraction with a relatively high boiling hydrocarbon oil. However, liquid-liquid extraction is only partially effective since in removing the co-boiling oils from the solvent, a portion of the high boiling oil dissolves in the liquid solvent. When solvent containing dissolved high boiling oil is returned to the primary extraction zone, the high boiling oil is transferred to the raffinate and contaminates the refined oil product. Although the dissolved high boiling oil can be removed from the solvent by distillation, this separation is costly since all of the solvent is removed as distillate from distilland comprising the dissolved high boiling oil.

In accordance with the process of this invention, at least a portion of the primary extract phase is extracted with a relatively high boiling hydrocarbon oil in vapor-liquid extraction to effect a high degree of separation of co-boiling oils from the solvent. The treating process of this invention is applicable to a wide range of hydrocarbon oils, for example, it may be applied to the manufacture of kerosenes, diesel fuels, gas-oil cracking stocks, light

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lubricating oil stocks, hydraulic oils, oils suited for the preparation of specialty products and oil suited for chemical manufacture. Although furfural is a preferred solvent useful in the process of this invention, other solvents may be employed particularly solvents which are partially miscible with water at about 100° F. and which are capable of forming an azeotrope with water. Such solvents include for example, other furans, nitrobenzene, amines for example, aniline, ketones, for example 3-pentanone and mesityl oxide, hydroxy compounds, for example phenol and n-amyl alcohol, aldehydes, for example, benzaldehyde, nitriles, for example propionitrile and butyronitrile, and esters, for example n-butyl acetate and n-amyl acetate. As is well known in the art, the solvent used may comprise a mixture of several individual solvents and the solvent may be modified by the inclusion of antisolvents, for example water.

In the vapor-liquid extraction step of this invention, separation of co-boiling hydrocarbons from the solvent in the primary extract is effected by vapor-liquid contact with a relatively high boiling hydrocarbon oil. Vapor-liquid extraction conditions are maintained by effecting contact of the vapor and liquid at a temperature above the boiling point of the solvent. The extraction tower may be heated for example by applying heat directly to the top of the tower or by preheating the high boiling extraction oil fed to the top of the tower. The high boiling oil preferentially dissolves the co-boiling oil so that solvent vapors substantially free of co-boiling hydrocarbons are removed overhead and substantially all of the oil initially dissolved in the solvent is removed in solution in the relatively high boiling oil as secondary extract. The relatively high boiling oil itself should be free of components boiling in the region of the solvent and preferably should consist of components having true boiling points at least 100° F. above the boiling range of the solvent. In some cases, the relatively high boiling oil may be used on a once through basis and discharged with the dissolved co-boiling oil in which case the boiling range of the two oils, that is the hydrocarbon oil feed and the relatively high boiling hydrocarbon oil, may overlap. Generally, however it is desirable to separate the dissolved oil as a separate product by distillation, in which case, the relatively high boiling oil should consist of components boiling wholly above the hydrocarbon oil feed. Suitable high boiling oils include both distillates and residua. A paraffinic residuum boiling wholly above 760° F. at atmospheric pressure is preferred for use as a relatively high boiling oil when treating hydrocarbon oil feeds boiling within the range of about 350 to 700° F. by ASTM distillation.

It is an object of this invention to provide a means of treating hydrocarbon oils containing constituents co-boiling with the solvent. Other objects will be apparent from the following description and claims. An advantage of the process of this invention is that the oil content of the solvent stream is maintained at a desirably low level thereby maintaining high solvent efficiency. Another advantage of this invention is that the oil content of the circulating solvent is maintained at a low level without requiring extremely high steam consumption. Another advantage of this invention is that separation of oil is effected without chilling or dilution and with a minimum of reconcentration of the solvent.

The accompanying flow diagram illustrates the process of this invention. Although the drawing illustrates one mode of practicing this invention, it is not intended to limit the invention to the particular apparatus or materials described.

Referring to the figure, a light lubricating oil stock is charged through line 1 to extraction tower 2. In extrac-

tion tower 2, the oil is countercurrently contacted with solvent introduced into the top of tower 2 through line 3. The solvent may suitably be wet furfural, that is, liquid furfural containing a small amount of dissolved water. Raffinate-mix, comprising refined light lubricating oil stock and a small amount of dissolved solvent is withdrawn through line 4 and passed to raffinate stripper 7. Water in the form of steam is introduced at the bottom of stripper 7 through line 8 in an amount sufficient to form an azeotrope with all of the solvent contained in the raffinate-mix thereby removing all of the solvent in the azeotrope withdrawn as distillate through line 10. Refined oil free of solvent is withdrawn from the bottom of stripper 7 through line 11.

The azeotropic mixture in line 10 comprises vapors of solvent, water, and a small amount of hydrocarbon oil. The vapor mixture is condensed in cooler 15 and the resulting condensate is passed through line 16 to separator 17. Three liquid phases separate, that is an oil phase containing a small amount of dissolved solvent and water, a water phase containing a small amount of dissolved solvent and oil, and a solvent phase containing a small amount of water and oil. Separator 17 is provided with internal baffles indicated by dotted lines 18 and 19 to permit separate withdrawal of the three phases. Separated solvent phase is withdrawn through line 20 and returned to extraction tower 2 through line 3. Separated water phase is withdrawn through line 21 for subsequent solvent recovery. Separated oil phase is withdrawn through line 22, passed to washer 23 and countercurrently contacted with water therein introduced through line 24. Oil free of solvent is withdrawn through line 25 and combined with the refined oil in line 11 to provide the solvent refined light lubricating oil stock product of the process. Water washings from washer 23 are withdrawn through line 26 and combined with the water phase in line 21 for subsequent solvent recovery.

Primary extract-mix comprising solvent and dissolved extracted oil is withdrawn from the bottom of tower 2 through line 30. Primary extract-mix is heated in heater 31 to a temperature substantially above the boiling point of the solvent to vaporize all of the solvent and a portion of the oil dissolved therein. The resulting vapor-liquid mixture is passed through line 32 to primary extract stripper 33. Stripper 33 is employed as a prefractionator and may be operated as a simple flash tower or may be provided with reboiler heat and reflux by conventional means not shown. Stripper 33 is operated to separate solvent containing co-boiling hydrocarbons as distillate from a bottoms product free of solvent. Bottoms from stripper 33 are withdrawn through line 34 as a part of the extract product of the process. Solvent vapor together with co-boiling hydrocarbon oil vapor is discharged from extract stripper 33 through line 49 to vapor-liquid extraction tower 50. Extraction tower 50 may be for example, a packed tower, a bubble tower, or other means known in the art for effecting vapor-liquid contact. A tower having a high length to diameter ratio is preferred. Contacting may be effected in a single stage or in multistages and on a continuous or batch basis. In extraction tower 50, the co-boiling hydrocarbon and solvent vapors are countercurrently contacted with a relatively high boiling hydrocarbon oil introduced into the top of tower 50 through line 55 at a temperature above the boiling point of the solvent. By contacting the solvent and co-boiling extract vapors with the liquid high boiling oil, the co-boiling oil vapors are condensed in the high boiling oil and solvent vapors free of oil are removed through line 56. A secondary extract comprising the high boiling oil, extracted co-boiling oil, and a small amount of dissolved solvent, is withdrawn through line 57 and passed to secondary extract stripping tower 58.

Steam is introduced through line 59 into the bottom of tower 58 in an amount sufficient to form the minimum boiling azeotrope with all of the solvent in the secondary

extract. All of the solvent is distilled overhead as azeotrope along with the co-boiling extract oil. High boiling oil is withdrawn from the bottom of tower 58 for recycle to vapor-liquid extractive distillation tower 50 through line 55. Co-boiling oil and azeotrope vapors removed as distillate from tower 58 are passed through line 65, cooler 66 and line 67 to separator 68. Separator 68 is provided with internal baffles indicated by dotted lines 69 and 70 to permit separation of the three liquid phases formed upon condensing the distillate from tower 58. Oil phase containing a small amount of dissolved water and solvent is withdrawn through line 72 and passed to extract washer 73. In washer 73 the oil is countercurrently contacted with water introduced through line 74. Water washings are withdrawn for solvent recovery through line 75 and washed oil is withdrawn through line 76 and combined with the extract oil product in line 34. Separated water phase is withdrawn from separator 68 through line 71, combined with water streams in line 21 and 75 and passed to fractionator 77 for recovery of dissolved solvent. Solvent phase is withdrawn through line 78 and recycled with the primary extract-mix in line 30 for solvent recovery.

Solvent vapors substantially free of oil in line 56 are condensed in cooler 80 and passed through line 81 to water-solvent settler 82. Water phase separating in settler 82 is withdrawn through line 83 and passed to fractionator 77 for recovery of dissolved solvent. Separated solvent phase is withdrawn from settler 82 through line 3 for charge to extraction tower 2.

Fractionator 77 is employed to recover solvent dissolved in water from the water discharged from the system. The water stream charged through lines 21, 26, 71, 75 and 83 contain dissolved solvent which is removed by distilling the minimum boiling azeotrope overhead through line 87. The azeotrope vapor stream is combined with the vapor stream in line 56 for condensation, separation of solvent phase, and return to the extraction system. Water free of solvent is withdrawn through line 88 for discharge from the system.

#### Example

The following example illustrates the application of the process of this invention to the refining of a light lubricating oil stock useful in the manufacture of hydraulic oils. In the following example, flow rates are expressed in terms of liquid barrels per hour regardless of whether the particular stream is in the liquid or vapor form.

A lubricating oil charge stock having a gravity of 30.9° API, an ASTM distillation initial boiling point of 440° F., a 50 percent point of 490° F., and an endpoint of 632° F. at a rate of 100 barrels per hour is countercurrently contacted with 263 barrels per hour of solvent having a composition of 90 percent furfural, 9 percent water and 1 percent oil in a primary extraction tower. Extraction is effected with a top tower temperature of 171° F. and a bottom tower temperature of 122° F. to produce 82 barrels per hour of raffinate mix and 281 barrels per hour of primary extract mix. Refined oil product at a rate of 69 barrels per hour is separated from the raffinate-mix for hydraulic oil manufacture.

Primary extract-mix at a rate of 281 barrels per hour comprising 80 percent furfural 12 percent extract oil, and 8 percent water together with 15 barrels per hour of recovered solvent as hereinafter provided comprising 75 percent furfural, 15 percent oil and 10 percent water are prefractionated effecting separation of 14 barrels per hour of stripped extract and 282 barrels per hour of overhead vapor. This overhead vapor includes all of the furfural and water and 58.3 percent of the oil in the prefractionator feed. This overhead vapor is passed to a vapor-liquid extraction tower operated at a top tower temperature of 380° F. A heavy paraffinic residual oil boiling wholly above 760° F. at atmospheric pressure is fed to the top of the extraction tower at a rate of 350 barrels per hour.

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Overhead vapor from the extraction tower is condensed to produce 253 barrels per hour of recovered solvent comprising 90 percent furfural, 9 percent water and 1 percent oil for recycle to the primary extraction tower.

Secondary extract-mix, at a rate of 379 barrels per hour comprising 6 percent extracted oil, 3 percent furfural and 91 percent heavy oil is withdrawn from the bottom of the vapor-liquid extraction tower.

Secondary extract-mix is stripped with steam to separate a bottoms fraction of heavy oil at a rate of 350 barrels per hour which is recycled to said vapor-liquid extraction tower. Secondary extract-mix stripper overhead is condensed forming oil, water, and furfural rich phases. An additional 16 barrels per hour of extract product is separated by water washing the oil. The furfural rich phase at a rate of 15 barrels per hour is recycled as said recovered solvent in admixture with said primary extract mix. Remaining furfural is recovered from solution in the collected water steams by azeotropic distillation.

I claim:

1. In the solvent refining of a feed hydrocarbon oil containing at least a small portion of constituents co-boiling with a liquid solvent wherein said feed hydrocarbon is contacted with said solvent in a liquid-liquid extraction zone forming separate primary extract and raffinate phases, the improvement which comprises vaporizing at least a portion of said primary extract phase forming a vapor comprising solvent and co-boiling hydrocarbon oil, contacting said vapor with liquid comprising a relatively high boiling hydrocarbon oil consisting of hydrocarbons having true boiling points at least 100° F. above the boiling range of said solvent in a vapor-liquid extraction zone, withdrawing solvent vapors free of co-boiling hydrocarbons as overhead vapor from said vapor-liquid extraction zone, condensing said overhead vapor forming a purified solvent stream for recycle to said solvent refining step, and withdrawing secondary extract comprising said relatively high boiling hydrocarbon oil and said co-boiling hydrocarbon oil from said vapor-liquid extraction zone.

2. The process of claim 1 wherein said solvent is at least partially miscible with water at 100° F. and is capable of forming an azeotrope with water.

3. The process of claim 1 wherein said relatively high boiling hydrocarbon oil consists of hydrocarbons boiling above the boiling range of said co-boiling hydrocarbon oil.

4. The process of claim 3 wherein said secondary extract is distilled separating said co-boiling hydrocarbon

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oil as overhead and said relatively high boiling hydrocarbon oil as bottoms for recycle to said vapor-liquid extraction zone.

5. The process of claim 2 wherein said secondary extract comprises solvent, said relatively high boiling hydrocarbon oil, and said co-boiling hydrocarbon oil, and said secondary extract is distilled in the presence of steam effecting separation of said co-boiling hydrocarbons and azeotrope of solvent and water as distillate and said relatively high boiling hydrocarbon oil as bottoms for recycle to said vapor-liquid extraction zone.

6. The process of claim 5 wherein said distillate is condensed forming separate oil, water, and solvent phases, co-boiling hydrocarbon oil is recovered from said oil phase, and said solvent phase is combined with said primary extract.

7. The process of claim 1 wherein said primary extract is prefractionated prior to said vapor-liquid extraction effecting separation of said vapor comprising solvent and co-boiling hydrocarbons, and distilland comprising extracted hydrocarbon oil free of solvent is withdrawn as prefractionator bottoms.

8. The process of claim 1 wherein said solvent comprises furfural.

9. The process of claim 1 wherein said co-boiling hydrocarbons comprise hydrocarbons having true boiling points in the region of the solvent boiling temperature and below.

10. The process of claim 8 wherein said relatively high boiling hydrocarbon oil comprises a paraffinic oil having an ASTM distillation initial boiling point of at least 625° F.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

2,216,932	10/40	Atkins	208—316
2,361,493	10/44	Patterson	208—313
2,576,172	9/51	Arnold et al.	208—313
2,685,556	8/54	Hachmuth	202—39.5
2,745,790	5/56	Manley	208—321
2,842,484	7/58	Fleck	208—313
2,908,731	10/59	Koble	208—313
2,909,576	10/59	Fenske et al.	208—313
2,936,283	5/60	Hutchings	208—313

##### FOREIGN PATENTS

476,610 12/37 Great Britain.

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