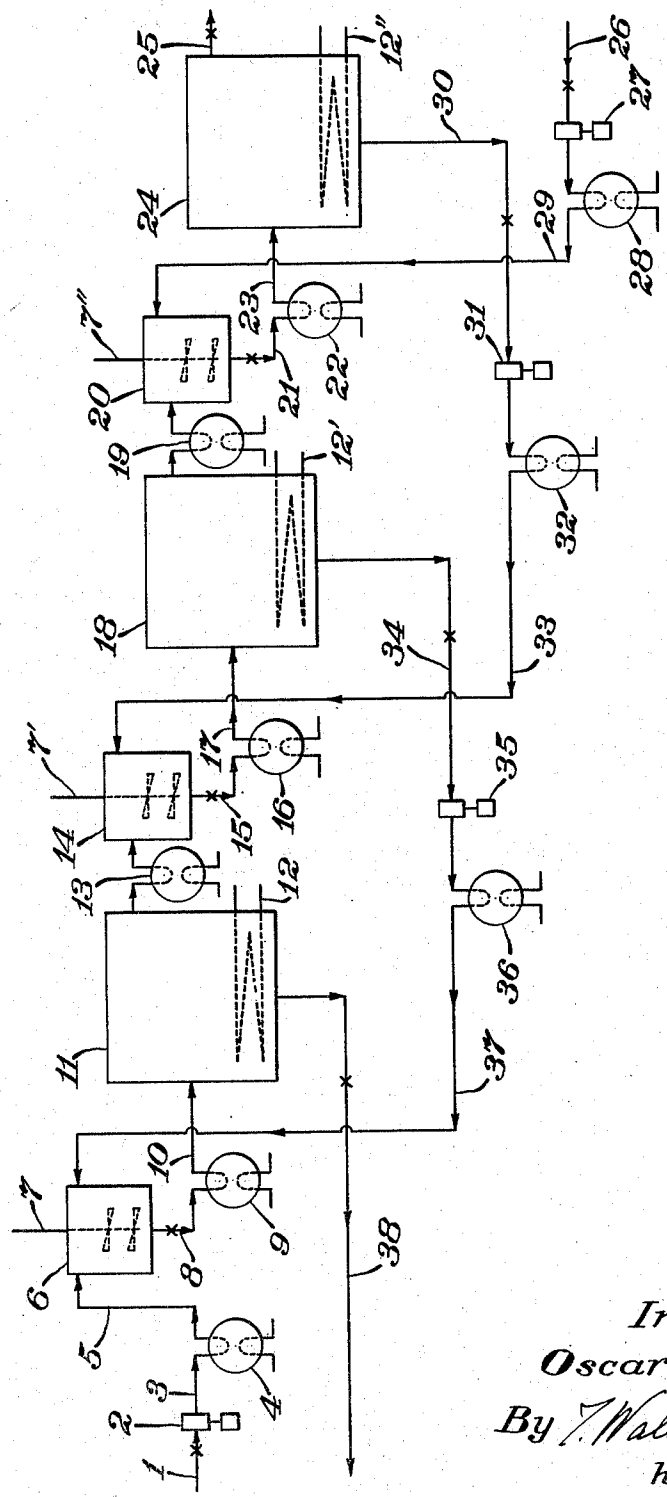
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HYDROCARBON OIL TREATMENT

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HYDROCARBON OIL TREATMENT

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The present invention relates to a process of obtaining countercurrent contact between partially immiscible liquids, and particularly to the extraction of components from hydrocarbon oils with a solvent which will selectively dissolve such components.

Heretofore, it has been found that certain selective solvents, as for example, nitrobenzene, phenol, and aniline and the like, may be used to effect the separation of a hydrocarbon oil, such as petroleum, into fractions of substantially the same boiling range but of different chemical compositions and of different physical properties. The difference in physical properties of the fractions so produced, i. e., the degree of paraffinicity or naphthenicity of the said fractions, may be expressed by the relationship of viscosity to gravity, for any particular oil. The viscosity-gravity constant, as developed by Hill and Coats in an article in Industrial and Engineering Chemistry, volume 20, page 641, 1928, will be used herein to indicate the degree of paraffinicity and of naphthenicity of the oil or oil fractions; the lower the value of the constant, the higher the degree of paraffinicity of the oil.

In accordance with the prior practice in the field of countercurrent solvent extraction, it has been customary to employ substantially the same temperature in each of the stages of a countercurrent extraction system or to employ a temperature gradient thruout the successive stages of such system. For example, in a 5 stage countercurrent system operated in accordance with the method first mentioned, each of the stages may be maintained at a temperature of the order of 15° C., or according to the second method, an increasing or decreasing temperature gradient of 5° C. between each stage may be maintained.

I have discovered that by adjusting the temperatures of the various stages so that the temperature of any stage is higher or lower than either of the stages next to or contiguous to the specified stage, I am able to obtain an increased yield of desirable oil of a given quality or the same yield of oil of a better quality than can be obtained in accordance with the prior processes. For example, in operating a 3 stage countercurrent extraction system employing a solvent such as nitrobenzene, I may maintain the 1st stage, i. e., that stage in which the oil stock is introduced in contact with partially used solvent, at a temperature of the order of 5° C.; the second stage at a temperature of 15° C., and 3rd stage, i. e., that from which the refined oil is discharged, at a temperature of 5° C.

It is believed that the type of temperature adjustment which I employ causes oil dissolved in some stages to be thrown out of solution in some preceding stages and sent in the direction of the stages in which such oil was dissolved. My process may be likened to that in a fractionating column in which the lower temperature stages function as dephlegmators to produce recycle or reflux oil which aids in increasing the efficiency of fractionation.

For purposes of illustration, reference is made to the accompanying drawing which shows diagrammatically, one form of apparatus suitable for carrying on my process:

In the drawing, a series of alternate mixing vessels 6, 14, and 20 and settling vessels 11, 18, and 24 are disposed in step-like arrangement, the mixing vessels being provided with paddle stirrers 7, 7', and 7'' respectively, or other suitable mixing devices, means for introducing thereinto oil and solvent, and means for passing the mixture therefrom into the respective settling vessels. The settling vessels are provided with heating and/or cooling coils 12, 12', and 12'' and means for passing undissolved oil to succeeding and solvent containing dissolved oil to preceding mixing vessels. The system is equipped with low pressure pumps, feed lines and heat exchangers so arranged as to maintain a regulated countercurrent flow of oil and solvent through the extraction stages, the heat exchangers 4, 9, 13, 16, 19, 22, 28, 32, and 36 controlling the temperatures of the oil and solvent streams, and indirectly the temperatures in the mixing and settling vessels.

In the operation of my process, I may choose, for example, nitrobenzene as the selective solvent and a lubricating oil as the stock to be selectively extracted. The oil stock supplied from a storage vessel (not shown) is drawn thru valve-controlled pipe 1, by means of pump 2, and is passed thru pipe 3 and heat exchanger 4 wherein it is cooled to the desired temperature, for example, 5° C. The cooled oil is then passed thru pipe 5 into mixing vessel 6. The selective solvent, i. e., nitrobenzene, is conducted from a storage vessel (not shown), thru valve-controlled pipe 26, and is passed by means of pump 27 thru heat exchanger 28 wherein it is cooled to the desired temperature, for example, 5° C. The cooled solvent is then passed thru pipe 29 into mixing vessel 20. After sufficient oil stock and solvent have been supplied to the system, a continuous countercurrent flow will be set up and the extraction process will commence to function. The oil stock charged to the mixing vessel 6, and the

partially spent solvent from the bottom of settling vessel 18, which flows thru valve-controlled pipe 34 and is forced by pump 35 thru heat exchanger 36 wherein it is cooled to about 5° C., is passed by means of pipe 37 into the mixing vessel 6, wherein it is contacted with the oil stock by agitation with the stirrer 7. The mixture of oil and solvent is passed thru valve-controlled pipe 8, heat exchanger 9 and pipe 10 into the settling vessel 11 and a separation of undissolved oil and solvent containing dissolved oil is effected at a temperature of about 5° C., the undissolved oil comprising the upper layer, and the solvent containing the dissolved oil the lower layer. The lower layer of spent solvent containing dissolved oil is withdrawn from the system by means of valve-controlled pipe 38 and the solvent and oil may subsequently be separated by distillation. The undissolved oil layer, containing a small quantity of solvent, occupies the upper portion of the settler 11, and flows by gravity thru heat exchanger 13, wherein it is heated to a temperature of, for example, 15° C., and thence into the mixing vessel 14. Vessel 14 is simultaneously supplied with partially spent solvent from the lower section of settler 24, which solvent flows thru valve-controlled pipe 30 and is forced by pump 31 thru heat exchanger 32, wherein it is heated to about 15° C. and thence is passed thru pipe 33 into said mixing vessel 14. The oil and solvent are herein again thoroughly contacted by means of stirrer 7', and the mixture of oil and solvent is passed by valve-controlled pipe 15 thru heat exchanger 16 and pipe 17 into settling vessel 18 wherein the separation into undissolved oil and solvent layers is effected at a temperature of about 15° C. The lower layer of solvent containing dissolved oil is withdrawn from settler 18 thru valve-controlled pipe 34 and is pumped thru heat exchanger 36 and pipe 37 into mixing vessel 6, as hereinbefore described. The undissolved oil layer in the upper portion of settler 18 flows by gravity thru heat exchanger 19, wherein it is cooled to a temperature of the order of 5° C., and thence into mixing vessel 20. Vessel 20 is simultaneously supplied with fresh solvent from a storage vessel (not shown), which solvent is passed thru valve-controlled pipe 26 and forced by pump 27 thru heat-exchanger 28, wherein it is cooled to about 5° C. and thence passed by means of pipe 29 into said mixing vessel 20. The oil and fresh solvent are herein thoroughly contacted by means of stirrer 7'', and the mixture of oil and solvent is passed by valve-controlled pipe 21 thru heat exchanger 22 and pipe 23 into settler 24 wherein the separation of undissolved oil and solvent layers is effected at a temperature of about 5° C. The lower layer of solvent containing dissolved oil is withdrawn from settler 24 thru valve-controlled pipe 30 and is passed to mixing vessel 14 as previously described. The upper layer of undissolved oil containing a small quantity of solvent is drawn from the upper portion of settler 24 and passed from the system by means of valve-controlled pipe 25. Such undissolved oil may subsequently be freed of traces of solvent by distillation. Thus, in accordance with the above described process, I am able to separate an oil containing paraffinic and naphthenic hydrocarbons into oil fractions respectively richer in paraffinic and naphthenic compounds, in a manner more efficient than any heretofore known.

While in the above illustration, I have described the mixing and settling operations in the 1st stage as effected at 5° C.; the 2nd stage at 15° C. and the 3rd stage at 5° C., I may operate the mixing vessels at temperatures of complete miscibility and thereafter adjust the temperatures of the mixer effluxes by means of heat exchangers 9, 16, and 22 prior to passing such effluxes to their respective settlers, which may operate at the aforementioned temperatures. Furthermore, while I have given the temperatures of 5° C., 15° C. and 5° C. as exemplary of suitable operating temperatures, I do not intend to limit myself thereto, but may employ various combinations of temperatures, depending upon the number of stages comprising the system, the character of the solvent and oil stock, the ratio of solvent to stock and the quality of the oil product desired. In the operation of a multi-stage system where the temperature of any particular stage is higher than that of either of the stages immediately adjacent thereto, such higher temperature stage may be sub-divided into sub-stages, each sub-stage being maintained at the same or higher temperature than the preceding sub-stage.

I do not intend to confine myself to a system comprising any definite number of stages, but contemplate as within the scope of my invention, any batch countercurrent system of 3 or more stages, or a continuous countercurrent system in a single stage, provided with alternate heating and cooling means. The following table will serve to illustrate the various temperature combinations which may be applied to a system of, for example, 7 stages.

Table 1

1st Stage	2nd Stage	3rd Stage	4th Stage	5th Stage	6th Stage	7th Stage
° C.	° C.	° C.	° C.	° C.	° C.	° C.
5	15	5	5	5	15	5
5	15	5	15	5	15	5
5	5	15	15	15	5	5
15	5	15	15	15	5	15
15	5	15	5	15	5	15
5	15	5	20	30	15	5

Table 2 presents a comparison of the results obtained in operating a 3 stage batch countercurrent system in which the temperature of each stage is the same; the temperature of each stage is successively increased; and the temperature of the intermediate stage is higher than that of either of the adjacent stages. Nitrobenzene was employed as the solvent and a residuum from Barbers Hill crude oil as the stock.

Table 2

Percent solvent based on stock	Temperature of ext'n stages			Undissolved oil fraction			
	1st	2nd	3rd	Percent yield	S. U. vis. @ 210° F.	A. P. I. gravity	Vis.-grav. constant
	° C.	° C.	° C.				
				100.0	123''	18.3°	0.876
200	5	5	5	38.0	89''	27.2°	0.813
200	5	10	15	39.3	93''	27.0°	0.814
200	5	30	5	40.3	92''	27.4°	0.810

Tables 3 and 4 present a comparison of the results obtained in operating a 3 stage batch countercurrent system in which the temperature of each stage is the same, in contrast to the operation of the same system in which the temperature of the intermediate stage is higher than that of either of the adjacent stages. Nitrobenzene

is employed as the solvent and the stocks treated were a vacuum distillate from a Mid-Continent crude oil and a residuum from Oklahoma crude oil respectively.

Table 3

Percent solvent based on stock	Temperature of ext'n stages			Undissolved oil fraction			
	1st	2nd	3rd	Percent yield	S. U. vis. @ 210° F.	A. P. I. gravity	Vis.-grav constant
	°C.	°C.	°C.				
				100.0	211″	21.7°	0.840
200	25	25	25	46.5	141″	27.9°	0.799
200	25	50	25	49.0	137″	27.9°	0.799

Table 4

Percent solvent based on stock	Temperature of ext'n stages			Undissolved oil fraction			
	1st	2nd	3rd	Percent yield	S. U. vis. @ 210° F.	A. P. I. gravity	Vis.-grav. constant
	°C.	°C.	°C.				
				100.0	142″	20.2°	0.858
150	5	5	5	55.0	99″	27.2°	0.810
150	0	25	5	58.7	95″	27.7°	0.808

It will be seen from the above tables, that, by my process of varying the temperature upwardly and downwardly from stage to stage in the extraction system, I am able to obtain an increased yield of oil of a given quality or the same yield of oil of better quality than may be obtained in accordance with the processes of the prior art.

The extent of the variation between temperatures in the different stages of the treating apparatus will vary with different oil stocks, solvents, etc., but in general is at least 5° C. between zones of different temperatures and in some instances may be 10° C. or more. In many cases it is desirable that the separating temperature in nonadjacent stages be substantially equal or at any rate should differ by not more than 5° or 10° C. The temperature of an intermediate stage should be removed from either of the nonadjacent stages by an amount at least as great as the variation between said nonadjacent stages.

While I have described my process in connection with the employment of nitrobenzene as a selective solvent, I do not intend to limit myself thereto, but may use any selective solvent or mixture of solvents, including, for example, any one or more of those mentioned by Ferris, Birkhimer and Henderson in their article appearing in Industrial and Engineering Chemistry, vol. 23, p. 753 etc. (1931).

What I claim is:

1. The process of extracting a hydrocarbon oil with a selective solvent, which comprises passing oil in countercurrent contact with the solvent through a plurality of extraction zones while maintaining the temperature in two non-adjacent zones substantially uniform with respect to one another and the temperature in a zone located between said two non-adjacent zones substantially different from the temperature in either of said two non-adjacent zones.

2. The process of extracting a hydrocarbon oil with a selective solvent, which comprises passing oil in countercurrent contact with the solvent through a plurality of extraction zones while maintaining the temperature in two non-adjacent zones within about 5° C. of each other and the temperature in a zone located between said two non-adjacent zones at least 5° C. different from that in either of said two non-adjacent zones.

3. The process of extracting a hydrocarbon oil with a selective solvent, which comprises passing oil in countercurrent contact with the solvent through a plurality of extraction zones while maintaining the temperature in two non-adjacent zones within about 10° C. of each other and the temperature in a zone located between said two non-adjacent zones at least 10° C. different from that in either of said two non-adjacent zones.

4. The process of extracting a hydrocarbon oil with a selective solvent, which comprises passing oil in countercurrent contact with the solvent through a plurality of extraction zones while maintaining an intermediate zone at a higher temperature than either of the zones adjacent thereto.

5. The process of extracting a hydrocarbon oil with a selective solvent, which comprises passing oil in countercurrent contact with the solvent through a plurality of extraction zones while maintaining an intermediate zone at a lower temperature than either of the zones adjacent thereto.

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