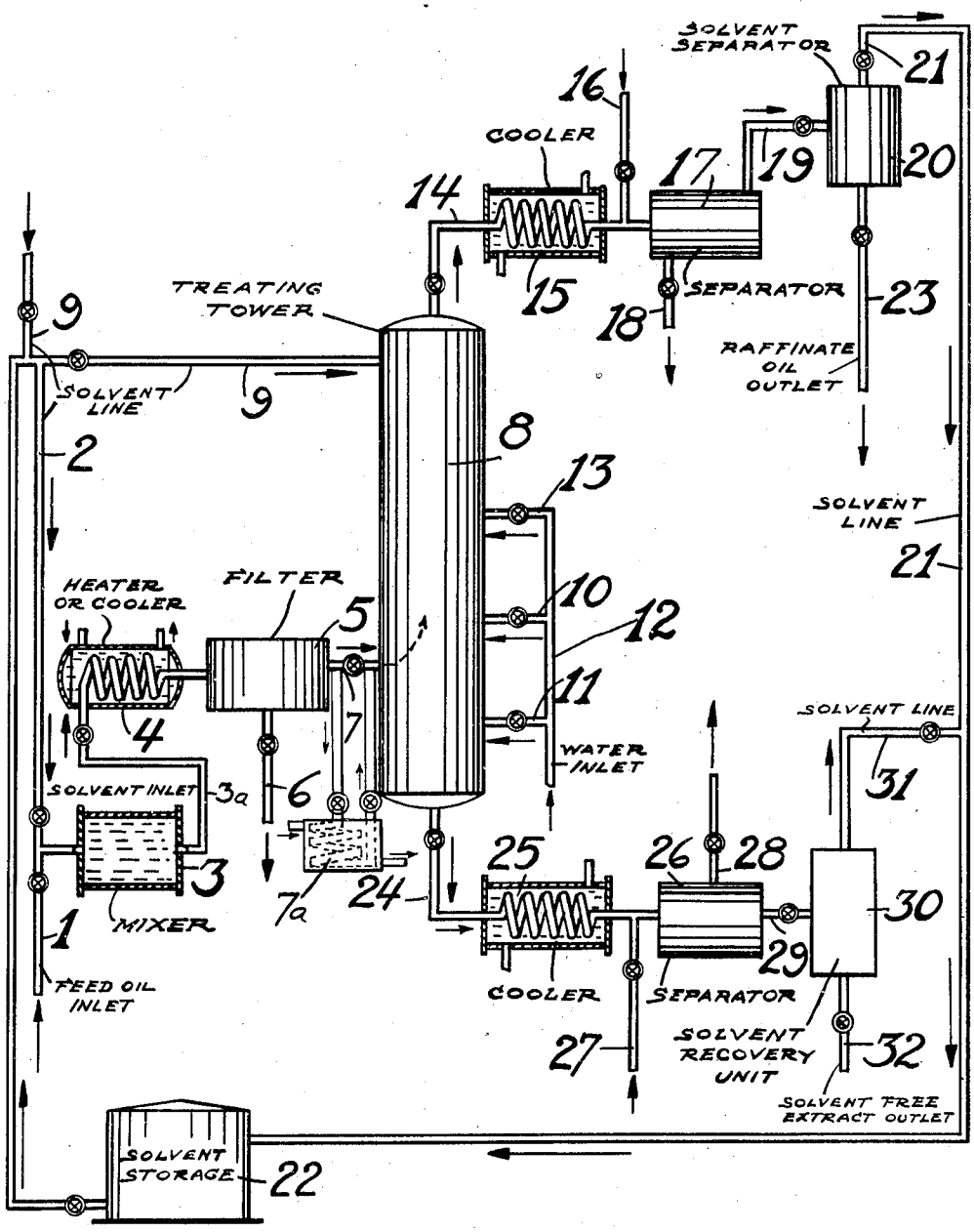
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REFINING OF MINERAL OILS

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REFINING OF MINERAL OILS

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The present invention relates to the refining of mineral oils. The invention is more particularly concerned with the segregation of petroleum oils into their relatively more paraffinic and into their relatively more aromatic constituents by means of selective solvents. In accordance with the process of the present invention, distinct improvements are secured in solvent treating operations by pretreating the feed oil in the presence of a relatively small amount of the selective solvent in a manner adapted to remove relatively minute quantities of substances which are entirely insoluble in the selective solvent under the conditions of operation and which would otherwise result in operating difficulties.

It is well known in the art to refine mineral oils and to segregate these oils into their relatively more aromatic and into their relatively more paraffinic constituents by means of various selective solvents. In processes of this character the general procedure is to extract the mineral oil with solvents of the class which have a preferential selectivity for the relatively more aromatic type compounds as compared to the relatively more paraffinic type compounds. Solvents of this character are, for example, furfural, phenol, sulfur dioxide, cresol, nitro benzene, aniline, beta beta dichlor diethyl ether, and the like. The oil and solvent or solvent mixture are mixed in various types of operations under temperature and pressure conditions adapted to form a highly aromatic or solvent extract phase and a highly paraffinic or raffinate phase. Although single or multi-stage treatments are employed, the preferred process is a countercurrent tower treating operation, since it is continuous and permits a more economical operation. In a countercurrent tower treating process the lighter phase, usually the oil, is introduced at the bottom or at the center section of the tower. This phase flows upwardly through the tower and intimately contacts the downflowing heavier phase, usually the solvent, which is introduced at or near the top of the tower. Complete mixing of the respective constituents is secured by suitable distributing and contacting means, such as distributing plates, pierced plates, contact masses, and the like. If the oil is the heavier phase, the conditions are reversed and the oil is introduced at the top of the tower, while the solvent is introduced at a lower section of the tower. In a countercurrent treating tower operation either the oil or the solvent may be the continuous phase, although it is generally preferred that the solvent be maintained as the continuous phase. The efficiency of a countercurrent treating tower operation is a function to a large extent of the efficiency of the contact between the respective phases, as well as upon the time of contact. However, when using certain solvents, particularly phenols, it has been found that certain oils contain constituents which cause extended emulsification of the solvent and oil. This greatly lowers the overall efficiency of the solvent treating operation, since the emulsification zones in effect decrease the effective area of the tower, resulting in a decrease in capacity and yields. My process, which comprises a pretreatment of the oil in the presence of a relatively small amount of the selective solvent, entirely eliminates emulsification and related operating difficulties and results in unexpected improvement in tower capacities and in products of improved quality.

The process of my invention may be readily understood by reference to the attached drawing illustrating one modification of the same. Feed oil, which for the purposes of description is taken to be a stock substantially free of asphalts and resins and boiling in the petroleum lubricating oil range is introduced into the solvent treating system by means of line 1. The feed oil is mixed with a relatively small amount of solvent, which for the purposes of illustration is assumed to be a phenol, which is introduced into line 1 by means of line 2. The mixture is passed through mixer 3, line 3*a*, heater or cooler 4, and then introduced into filtering means 5 which may comprise centrifuges, press filters, or equivalent filters arranged in any desirable manner. A relatively small amount of oil constituents which are insoluble in the phenol are withdrawn from pre-treatment unit 5 by means of line 6. The feed oil, together with the relatively small amount of the phenol, is withdrawn from filtering means 5 by means of line 7, and if desired through line 7*a* in order to heat it or cool it to the optimum tower countercurrent treating temperature, and introduced into main solvent treating unit 8, which for the purposes of description is assumed to be a countercurrent treating tower. The feed oil flows upwardly through tower 8 and countercurrently contacts substantially the entire quantity of phenol which is introduced into countercurrent treating tower 8 by means of line 9. Efficient contact between the countercurrently flowing phases is secured by adequate contacting means such as distributing plates, contacting masses, pierced plates, and

the like. The selectivity and solvent power of the selective solvent may be adjusted to any desired degree by the instroduction of a solvent modifying agent such as water into tower 8 by means of lines 10, 11, 12, and 13. Temperature and pressure conditions are adapted to secure the formation of a highly paraffinic or raffinate phase which is withdrawn from tower 8 by means of line 14. This phase may be cooled in cooler 15 or mixed with a solvent modifying agent which is introduced by means of line 16 in order to secure a further phase separation in separator 17. The precipitated solvent rich phase is withdrawn from separator 17 by means of line 18 and handled in any manner desirable. This phase may be returned to the countercurrent treating tower or utilized as an intermediate stream. Under certain conditions it may be desirable to use this phase relatively rich in solvent to dilute the feed oil prior to pretreating the same. The relatively solvent poor phase is withdrawn from separator 17 by means of line 19 and passed to solvent separator 20 in which the solvent is removed by means of line 21 and returned to solvent storage 22. A solvent-free raffinate oil is withdrawn by means of line 23 and removed from the system.

The solvent extract phase may be similarly handled. This phase is withdrawn from tower 8 by means of line 24 and may be cooled in cooler 25 in order to secure a further phase separation in separator 26. Phase separation may be aided or entirely secured by the addition of a solvent modifying agent which is introduced by means of line 27. The precipitated phase is withdrawn from separator 26 by means of line 28 and handled in any manner desirable. This phase may be returned to the countercurrent treating system or removed as an intermediate product. The solvent rich phase is withdrawn from separator 26 by means of line 29 and passed to solvent recovery unit 30 from which the solvent is removed by means of line 31 and returned to solvent storage 22. A solvent-free extract is withdrawn from unit 30 by means of line 32, removed from the system, and handled in any manner desirable. Under certain conditions it may be desirable to utilize a small amount of the relatively solvent rich phase withdrawn from line 29 by means not shown to dilute the feed oil prior to pretreating the same.

The process of the present invention may be widely varied. Although the operation may be applied in the treatment of any feed oil, it is particularly applicable in the treatment of oils which are substantially free of asphalts and resinous materials. The feed oils, in general, are treated in a manner to remove the relatively small quantity of oil constituents which are entirely insoluble in the selective solvent and which position themselves between the interfaces and thus cause considerable difficulty in the attainment of equilibrium conditions between the respective phases. These difficulties are generally measured in terms of emulsification. In general, I have found that these constituents comprise less than about 2% of the feed oil and are generally in the range from 0.01% to 0.5% of the feed oil.

The amount of solvent introduced in the charge oil before pretreating the same may vary widely. The quantity will depend upon the particular solvent being used and the character of the feed oil being solvent treated, as well as upon the temperature of the oil. In general, it is desired to introduce sufficient solvent into the charge oil to approximately saturate the oil with solvent which results in the precipitation of substantially all of the solvent insoluble oil constituents without the formation of two phases containing an appreciable amount of the selective solvent. For example, when using phenol, I have found that it is desirable to dilute the oil with from about 5% to 20% of phenol, preferably from 10% to 12% of phenol before pretreating the same. This results in the precipitation of about 0.01% to 0.5% of solvent insoluble constituents. The temperature of the pretreatment may likewise vary considerably. In general, the temperature is preferably in the range below about 150° F. depending upon the particular solvent employed. The pretreated oil after removal of the solvent insoluble constituents is then heated or cooled to optimum tower countercurrent treating temperatures. When employing phenol as the selective solvent in the treatment of petroleum oils boiling in the lubricating oil range, I have found that it is particularly desirable to approximately saturate the oil with phenol at a temperature in the range below about 110° F. to 125° F. under conditions to precipitate a relatively small per cent of solvent insoluble oil constituents without the formation of two phases containing an appreciable amount of the selective solvent. Feed oil is then filtered to remove the insoluble constituents and then heated to optimum countercurrent treating temperatures generally in the range from about 150° F. to 225° F.

In order to further illustrate the invention, the following example is given which should not be construed as limiting the invention in any manner whatsoever:

Example

A lubricating oil having a viscosity of 135 Saybolt at 210° F., a gravity of 24.4° A. P. I. derived from Rodessa crude and which had been previously acid treated and steam sweetened to remove the asphaltic constituents was solvent treated with phenol in various operations. In the first operation the feed oil was passed directly into a countercurrent treating tower. In a second operation the feed oil was filtered using centrifuges and then passed into the countercurrent treating tower. In a third operation a propane precipitated oil was passed directly into a countercurrent treating tower. In a fourth operation conducted in accordance with the process of the present invention the feed oil was saturated with phenol, filtered by means of press filters and then passed into the countercurrent treating tower. The results of these operations were as follows:

	Per cent phenol insoluble oil material in oil feed	Maximum tower capacity; volumes of oil feed per hour	Per cent capacity based upon operation 4
Operation 1	0.24	400	13.3
Operation 2	0.13	620	20.7
Operation 3	0.03	2,300	76.6
Operation 4	0.01	3,000	100.0

From the above data it is apparent that material unexpected advantages are secured by pretreating the oil in the manner described in accordance with the present invention.

The process of the present invention is not to be limited by any theory or mode of operation, but only in and by the following claims in which

it is desired to claim all novelty in so far as the prior art permits.

I claim:

1. In a process for segregating into its relatively more aromatic and into its relatively more paraffinic constituents a viscous petroleum lubricating oil substantially free of asphalts, which tends to develop emulsification difficulties during solvent extraction, due to the presence in said oil of a small amount, less than 2%, of dissolved material which precipitates out during solvent extraction in the form of a finely divided insoluble solid which distributes itself between the interfaces of the solvent and oil, the improvement comprising subjecting said oil to preliminary treatment at a temperature between about 110° F. and 150° F. with a solvent having a preferential selectivity for the relatively more aromatic compounds as compared to the relatively more paraffinic compounds, using only an amount of said solvent, between the approximate limits of 5% and 20% by volume, to approximately saturate said oil therewith but insufficient to cause the formation of two liquid phases, whereby a small amount of material precipitates out of said solvent-oil solution as a filterable solid phase, removing said precipitated solids by filtration, and then subjecting the filtered oil to solvent extraction with a large enough volume of the same selective solvent and under suitable temperature conditions to cause the formation of two liquid phases.

2. In a process for the segregation into its relatively more aromatic and into its relatively more paraffinic constituents a viscous petroleum lubricating oil having a viscosity of about 135 seconds Saybolt at 210° F. and a gravity of about 24.4° A. P. I., derived from a Rodessa crude oil, and which had been previously acid-treated to remove asphaltic constituents, which comprises mixing with said oil at a temperature of about 110° to about 125° F. a sufficient amount of phenol, between about 5% and about 20%, to approximately saturate said oil therewith but insufficient to cause the formation of two liquid phases, to precipitate a small amount, less than 0.5% of the feed oil, of phenol-insoluble constituents as a filterable solid phase, filtering said oil in a press filter to remove said solid precipitate and to produce a filtered oil free from emulsifying tendencies when subjected to phenol extraction, and then countercurrently extracting said filtered oil with phenol at a temperature of about 150° F. to 225° F.

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