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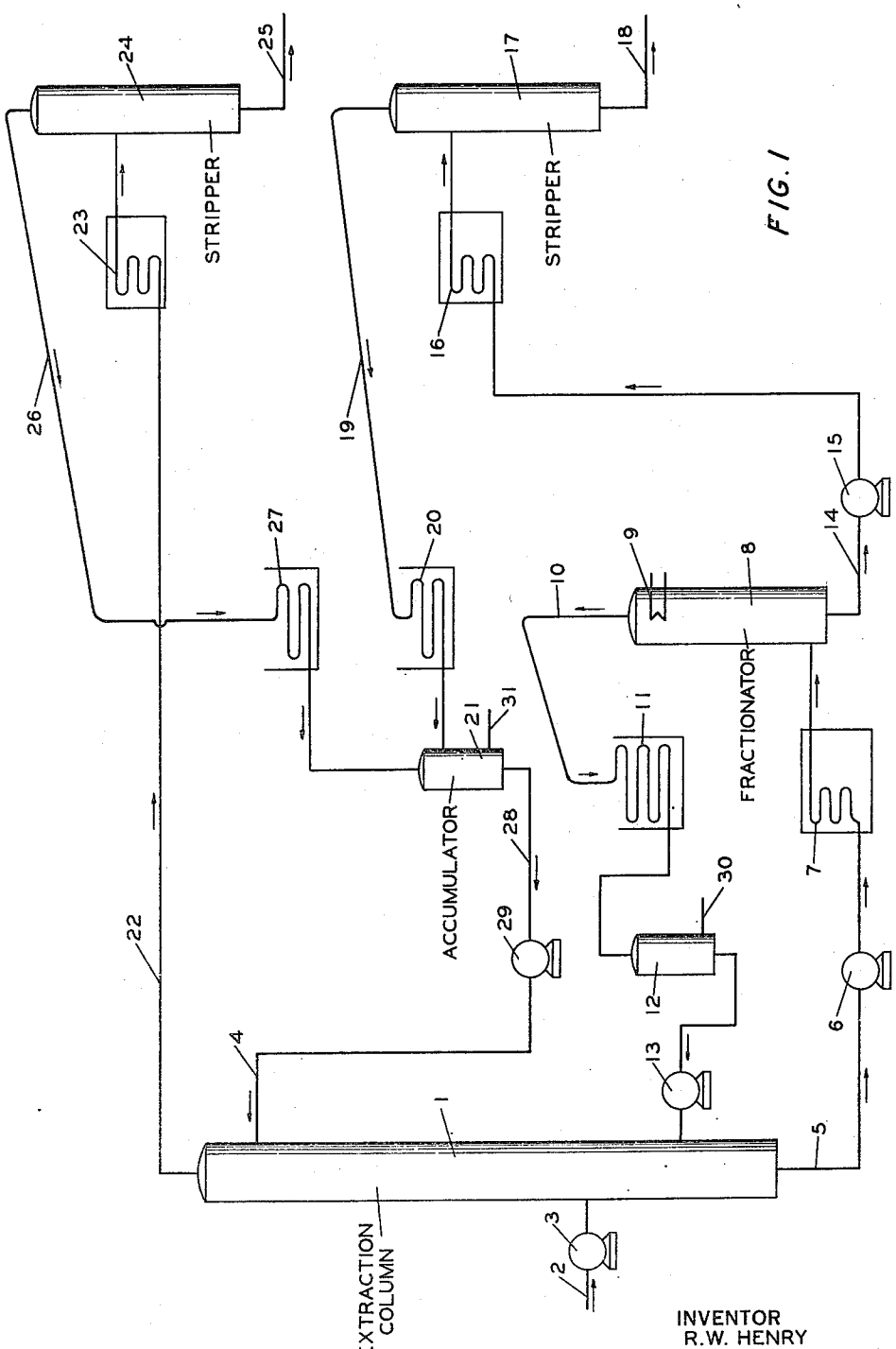


FIG. 1

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SOLVENT EXTRACTION OF OILS

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This invention relates to an improved process for preparing, purifying and improving mineral oil by solvent extraction.

Solvent extraction refers to the separation of a liquid mixture into component parts by treatment with an immiscible solvent in which one or more of the components are soluble. The solvent and solution are contacted, the resultant phases separated, and the solvent recovered from each phase. The phase containing the solvent and its dissolved solute is termed the "extract," while the phase containing the undissolved components is termed the "raffinate." As applied to petroleum, and particularly to lubricating oils, solvent extraction usually means the separation of desirable paraffinic components of the lube oil stock from the naphthenic or other undesirable components by treatment with a solvent. Solvent extraction processes for refining lubricating oils have undergone rapid development within the past few years. The chief value of these processes is their ability to produce high viscosity index oils from mixed base oil stocks. The solvent used must necessarily, therefore, be a good solvent for the naphthenic and other undesirable components and a poor solvent for the paraffinic components, or vice versa. Of the former type of solvents, many are known in the art; for example, furfural, nitrobenzene, phenol, crotonaldehyde, "chlorex," cresylic acid, and pyridine.

Various types of extraction systems, such as single contact, multiple-contact, countercurrent multiple-contact, and continuous countercurrent are well known in the art. It is known that solvent extraction is comparable to fractionation in that rectification may be accomplished by suitable refluxing. Such rectification has been accomplished by returning a portion of the extract or raffinate to the extraction system as "backwash" or by gradation of temperature between the ends of the system. Refluxing has been for the purpose of decreasing the amount of solvent required or improving the separation of paraffinic from naphthenic components, or both.

There are numerous disadvantages of refluxing by these methods. In the case of backwashing, the reflux is obtained by supersaturation of the solvent solution which decreases the natural selectivity of the solvent. Extract oils are naturally unstable hydrocarbons which tend to darken or otherwise deteriorate during heating to strip them of solvents. Returning these extract oils to the system increases the concentration of colored and unstable materials in the solvent, lowering the quality of the raffinate oil produced and decreasing the effectiveness of the system. Gradation of temperature between the ends of the system involves refrigeration which is expensive in operation. Low temperature operation makes the raffinate phase viscous and difficult to handle. A further disadvantage of low temperatures is entrainment of both phases in the form of a slurry by wax precipitated from the oil. In practicing the invention herein disclosed, effective rectification is attained without the disadvantage of pumping back a portion of the extract or raffinate oil and without the use of refrigeration with its inherent disadvantages.

An object of this invention is to provide an improved process for solvent treating mineral oils.

A further object of this invention is to provide a process for increasing the efficiency of solvents for extraction purposes.

A further object is to provide means for securing and controlling a refluxing action in solvent extraction which effectively improves the sharpness of separation between components of the solution being treated.

A still further object is to provide a highly adaptable, flexible process for separating asphaltic, naphthenic, and other undesirable components from mineral oil stocks.

A still further object of the present invention is to secure refluxing action in solvent extraction without the deleterious effects of backwashing and without the necessity of adding and later separating diluents or precipitants from the solvent.

Other objects and advantages of the invention will be apparent during the course of the following description.

The figure is a flow diagram illustrating a preferred manner of carrying out the present invention.

Referring to the figure, the numeral 1 refers to a countercurrent extraction column in which the two liquid phases are passed continuously in opposite directions, the flow resulting from the difference in density of the two phases. Oil stock to be treated is introduced through line 2 and pump 3 into the extraction column near its middle where it comes in contact with downwardly flowing solvent introduced near the top of the column through line 4. The extract phase, consisting of naphthenic solvent containing dissolved oil, is withdrawn from the bottom of the column through line 5 to pump 6 from which it passes through heater 7 to fractionator 8 having means of reflux, such as cooling coil 9 at its top. Vapors from fractionator 8 pass through line 10 to condenser 11 where they are condensed and the resulting liquid cooled and passed to accumulator 12 before being introduced into the lower part of tower 1 by pump 13. Liquid from the base of fractionator 8 is withdrawn through line 14 and pump 15 from which it passes through heater 16 to stripper 17. Extract oil from the base of stripper 17 passes through line 18 to storage, or to further processing. Solvent vapors leaving

stripper 17 through line 19 are condensed and cooled in condenser 20, and collected in accumulator 21.

The raffinate phase, consisting of paraffinic oil, together with some dissolved solvent, flows from the top of extraction column 1 through line 22 and heater 23 into stripper 24. Raffinate oil is removed from the bottom of the stripper through line 25 to storage, or further processing. Solvent going overhead from the stripper passes through line 26 and condenser 27 to accumulator 21 where it is mixed with the overhead from stripper 17. The mixture from accumulator 21 is withdrawn by means of pipe 28 and fed by pump 29 to the upper part of column 1 through line 4. For control of the composition of the mixture of solvent and diluent at the upper and lower portions of the tower, accumulators 12 and 21 have connections 30 and 31, respectively, for adding or withdrawing solvent mixture in starting up the process or intermittently when due to losses encountered in practical operation.

It is to be understood that any solvent or combination of solvents and/or any diluent or combination of diluents may be used in applying the present invention. For example, pyridine, or a mixture of pyridine homologs containing picolines and similar materials, plus regulated quantities of water or other diluent, such as methanol, ethanol, isopropyl alcohol, or similar material gives good results when used for the solvent treating of mineral oils in the manner described herein. In its pure state pyridine possesses a high miscibility with oil, making it necessary to operate an extraction system utilizing the undiluted solvent at very low temperatures. In carrying out the present invention, the solvent is rendered less miscible with the oil by the use of a diluent.

Solvent mixtures of pyridine or pyridine homologs with water exhibit a minimum in their boiling point curves. If such a mixture is heated to the boiling point, and the vapors rectified, a mixture of pyridine or pyridine homologs and water will be obtained as the product of the distillation. This mixture is approximately 40% water and 60% pyridine or pyridine homologs, and boils at approximately 200° F., whereas pure pyridine boils at 240° F., and pyridine homologs boil at somewhat higher temperatures. In the case of a solvent mixture of pyridine, and pyridine homologs, containing small amounts of methanol, ethanol, iso-propyl alcohol, and similar materials, these diluents are of lower boiling points than pyridine and therefore, when such a mixture is heated to the boiling point and the vapors rectified, the distillate obtained is rich in diluent. In either case, this distillate, being rich in the diluent, has a lower solvent power for mineral oil than the original mixture of pyridine and diluent, or pyridine homologs and diluent.

In operation, charge oil enters the system through line 2 and is introduced at a point near the middle of column 1. Solvent is introduced through line 4 at the top of the column. This solvent contains a sufficient quantity of diluent to render it immiscible with the charge oil at the operating temperature and will be referred to hereinafter as solvent A. It is preferable to use a solvent which has a miscibility temperature with the charge oil of about 140–150° F., when operating the column at a temperature of 100° F., but it is not desired to be limited by these temperatures since the system will function successfully over a much wider range, as from 10 to 100° F. difference between the miscibility and the operating temperatures. Miscibility temperature of the solvent with the oil is controlled by regulating the amount of diluent in the solvent, the miscibility temperature increasing with an increase in percentage of diluent added. The quantity of solvent and oil in extraction tower 1 is preferably controlled so as to be approximately in the ratio of four parts of solvent to one part of oil. However, this ratio is subject to a much wider variation. Under the operating conditions, a portion of the raffinate oil layer in the top of extraction column 1 is dissolved by the downwardly flowing solvent. This dissolved oil is the most naphthenic portion of the oil in contact with the solvent. The solvent and dissolved oil pass downwardly through extraction column 1 to the lower portion of the column where they come in contact with a second solvent, hereinafter designated as solvent B, entering the column from pump 13. The downwardly flowing solvent A has a higher solubility for oil and a lower percentage of diluent than that of solvent B. Solvent B causes the precipitation of a portion of the oil which had been dissolved in the solvent extraction column. This precipitated oil is the most paraffinic portion of the oil which was in solution. The precipitated oil flows upwardly through the extraction column in the form of small droplets, the upward movement being due to the difference in the specific gravity of the precipitated oil and of the naphthenic solvent containing extract. As this oil flows upwardly through the extraction column, countercurrent to downwardly flowing naphthenic solvent containing dissolved oil, the equilibrium between the naphthenic component of the dissolved oil and precipitated oil continually changes with the result that the downwardly flowing solvent continually releases a portion of its dissolved oil, such portion being the most paraffinic part of the oil, and in its place, dissolves the most naphthenic portion of the upwardly flowing precipitated oil. In this manner the upwardly flowing oil becomes increasingly paraffinic in nature as it approaches the top of the extraction tower and the dissolved oil becomes increasingly naphthenic in nature as it approaches the bottom of the extraction tower. It is readily apparent that the longer the path through which the upwardly flowing precipitated oil passes in countercurrent to the downwardly flowing solvent and dissolved oil, the greater the degree of rectification obtained.

The solvent phase withdrawn from the base of column 1 is passed first to fractionator 8 where a portion of the solvent is recovered from the extract and finally to stripper 17 where the remainder is removed. Distillate obtained from fractionator 8 (solvent B) is rich in diluent, approaching a composition corresponding to that of the minimum boiling mixture for the particular solvent and diluent being used. By proper regulation of the reflux control in the top of fractionator 8, rectification of solvent distillate may be varied, and in this manner the quantity of solvent B introduced into column 1 may be so regulated as to produce the desired quantity of precipitated oil. The rate at which solvent and dissolved extract are withdrawn from the bottom of column 1 is dependent upon the quantity of extract yield desired, the percent of diluent present in the section of the tower below the introduction of solvent B, and the temperature of operation. By careful regulation of these conditions,

the percentage of extract dissolved in solvent may be kept at a low value which results in high selectivity of the solvent. By withdrawing a dilute solution from the bottom of column 1, the ratio of solvent to oil may be increased, giving a large quantity of downwardly flowing solvent in the column. This large quantity of downwardly flowing solvent creates a current against which the precipitated oil and raffinate phase must flow. The rate of flow of solvent downwardly may be controlled and offers means of controlling the rate of upward flow of precipitated oil. Increasing the rate of flow of the solvent downwardly decreases the rate of flow of oil upwardly, thereby increasing the length of path through which the upwardly flowing oil must travel to reach the top of the tower and results in a better separation of components. Solvent leaving the extraction column with the raffinate is recovered by stripper 24. This recovered solvent is mixed in accumulator 21 with the solvent recovered from the extract by stripper 17 and the mixture is introduced at the top of the extraction column as solvent A.

We have successfully operated a solvent extraction process of this type under the following conditions: Solvent A entering the top section of the extracting column was commercial pyridine containing 3% water as a diluent. This mixture was miscible at 180° F., with the oil being extracted. The temperature at the top of the column was 120° F. Solvent B, having a composition corresponding to the pyridine-water minimum boiling point mixture, was introduced near the base of the extraction column in a sufficient quantity to give a resulting solvent analyzing 6% water at that point. The miscibility temperature of this 6% water solution was 350° F.; temperature at the bottom of the column was 80° F. With conditions as above, at the top of the column, if refrigeration alone were used at the bottom to produce the same reflux, the bottom temperature required would have been minus 90° F. This follows from the fact that the quantity of oil dissolved by the solvent is a function of the difference between the existing temperature and the miscibility temperature of the solvent-oil mixture. Solvent B can of course contain any amount of water less than the constant boiling mixture down to the neighborhood of 6% water. The optimum operating condition, however, is the constant boiling mixture in the case of water, or nearly those proportions in the case of other diluents which do not have a constant boiling mixture with pyridine.

The process may be applied to multiple-contact extraction in which the extraction column is replaced by a series of mixers and separators, solvent B being introduced into a stage, or into each of several stages, near the extract-oil end of the series, and solvent A being introduced into the stage at the raffinate-oil end of the series. Other applications will be apparent to those skilled in the art.

The foregoing examples and illustrations are not to be interpreted as limiting our invention, but are intended as examples of the flexibility and general utility of our process.

We claim:

1. The method of refining and purifying mineral oil to separate the asphaltic and other undesirable bodies from the relatively more desirable paraffinic portion of the oil which comprises adding commercial pyridine as the selective solvent to the hydrocarbon mixture in an extraction zone, adding a constant boiling point mixture of water and commercial pyridine to the solution in the extraction zone as a precipitant to cause a refluxing action, thereby separating the pyridine and oil solution into a more desirable raffinate phase and a less desirable extract phase, withdrawing the extract phase from the extraction zone, fractionating the extract phase to obtain a constant boiling point mixture of water and commercial pyridine having approximately 40% of water in the mixture and returning the fractionated mixture to the extraction zone for further refluxing.

2. The method of refining and purifying mineral oil to separate asphaltic and other undesirable bodies from the relatively more desirable paraffinic portion of the oil which comprises treating the hydrocarbon mixture with a preferential solvent composed of commercial pyridine and with a constant boiling point mixture of water in commercial pyridine, in which a stream of the commercial pyridine is passed through an extraction zone having initial and final points, the liquid hydrocarbon mixture to be treated being introduced into the extraction zone at an intermediate point whereby the non-paraffinic components are selectively dissolved in the solvent together with some of the paraffinic components, the dissolved components moving in the same direction as the stream of solvent, the undissolved components moving countercurrently to the first mentioned stream, the improvement comprising withdrawing the extract phase at the final point of the extraction zone, fractionating the extract phase to obtain the constant boiling point mixture of water in commercial pyridine, and a commercial pyridine-extract bottoms, and returning the constant boiling point mixture to the extraction zone at a point adjacent the final point to precipitate dissolved paraffinic components to serve as reflux.

3. The method of refining and purifying mineral oil to separate asphaltic and other undesirable bodies from the relatively more desirable paraffinic portion of the oil which comprises treating the hydrocarbon mixture with a preferential solvent composed of a fraction of commercial pyridine and with a constant boiling point mixture of water in a fraction of commercial pyridine, in which a stream of the fraction of commercial pyridine is passed through an extraction zone having initial and final points, the liquid hydrocarbon mixture to be treated being introduced into the extraction zone at an intermediate point whereby the non-paraffinic components are selectively dissolved in the solvent together with some of the paraffinic components, the dissolved components moving in the same direction as the stream of solvent, the undissolved components moving countercurrently to the first mentioned stream, the improvement comprising withdrawing the extract phase at the final point of the extraction zone, fractionating the extract phase to obtain the constant boiling point mixture of water in a fraction of commercial pyridine, and a commercial pyridine-extract bottoms, and returning the constant boiling point mixture to the extraction zone at a point adjacent the final point to precipitate dissolved paraffinic components to serve as reflux.

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