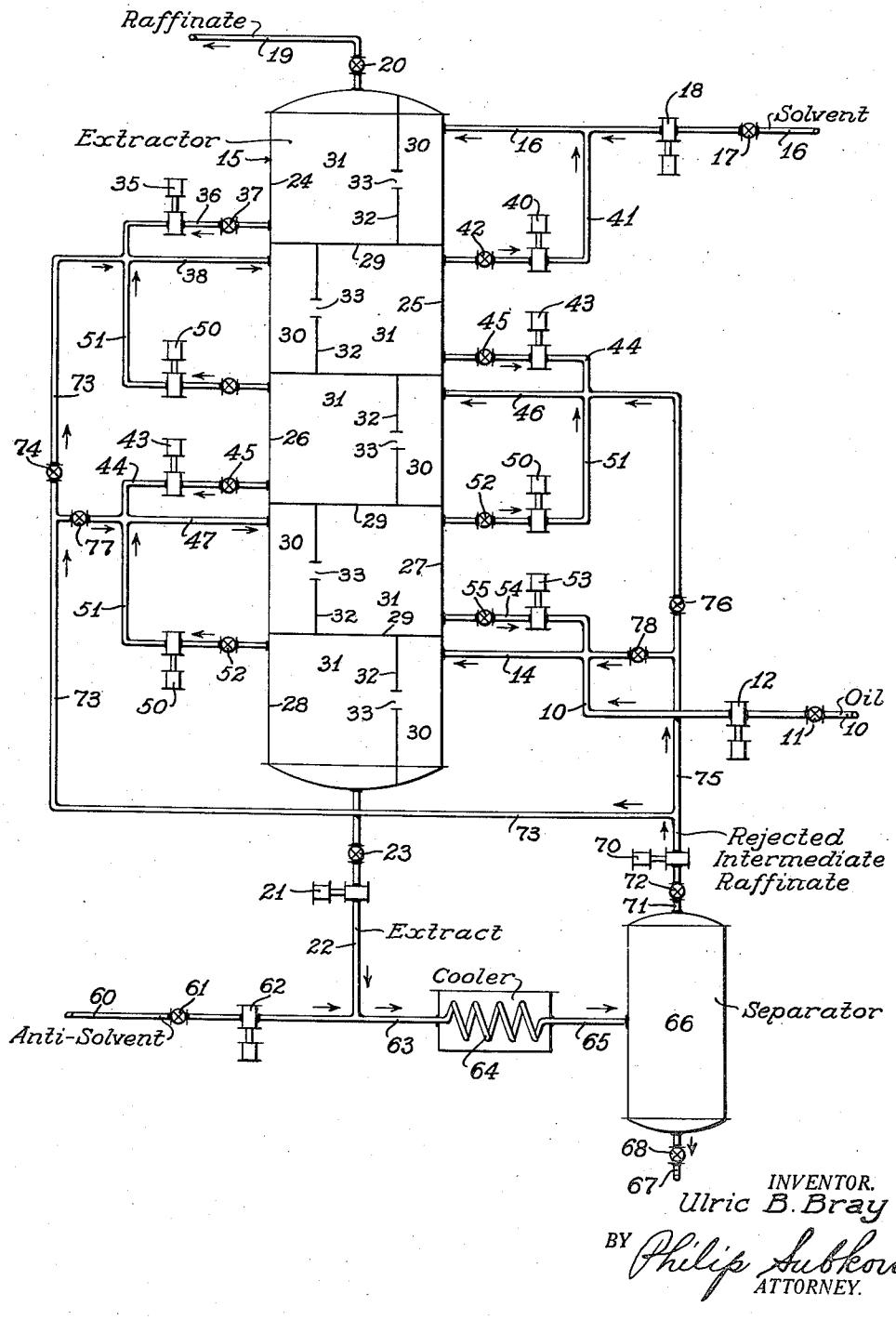
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PROCESS FOR SOLVENT EXTRACTION OF OILS

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PROCESS FOR SOLVENT EXTRACTION OF OILS

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This invention relates to the extraction of oils by employing a selective solvent. Although applicable to the treatment of other oils, it refers more particularly to the production of lubricating oil by a selective solvent extraction process.

It has been found that desirable paraffinic hydrocarbons can be separated from the undesirable olefinic, naphthenic and/or aromatic compounds by the use of solvents which selectively dissolve the undesirable hydrocarbons but which exhibit only a very limited solvent power upon the desirable paraffinic hydrocarbons.

When I use the term "paraffinic hydrocarbons" I mean those highly saturated compounds which are present in petroleum and which are characterized by a low temperature viscosity susceptibility, i. e. they exhibit a minimum change of viscosity for a given change in temperature. They also are characterized by relative stability to air and sunlight, exhibiting little tendency toward discoloration or sludge formation. This definition is not meant to include those compounds which are usually solid or semi-solid at ordinary temperatures and which are known as "wax" or "petrolatum"; but, of course, it is obvious that my invention is meant to also include the selective extraction of waxy oils. As a matter of convenience hereafter, I will refer to the undesirable components, such as olefinic, naphthenic and/or aromatic hydrocarbons, as the "non-paraffinic" components of petroleum. These fractions are characterized by a relatively high temperature viscosity susceptibility and are relatively unstable to air and sunlight, exhibiting discoloration and sludge formation.

A further indication of the purity of a lubricating oil is its viscosity gravity constant. This constant represents the paraffinicity or naphthenicity of an oil. A high value represents a high degree of naphthenicity while low values indicate relatively greater paraffinicity. Lubricating oils from natural crudes range from 0.903 viscosity gravity constant for an extreme Gulf Coast type to 0.807 for an extreme Pennsylvania type or even beyond. The viscosity gravity constants referred to in this application have been determined by the method employed by Hill and Coates as set forth in the Journal of Industrial and Engineering Chemistry, vol. 20, page 641 of 1928. The "paraffinic" hydrocarbons to which I refer hereinafter are characterized by relatively low viscosity gravity constant, while the "non-paraffinic" constituents of petroleum are characterized by relatively high viscosity gravity constant.

A number of selective solvents for extraction have been found; for example, it has been shown that such materials as aniline, chloraniline, nitrobenzene, dichlorethyl ether, phenol, chlorophenol, cresol, sulphur dioxide commingled with benzene, and furfural are highly selective as solvents for the non-paraffinic hydrocarbons. When these solvents are commingled with petroleum or petroleum fractions under the proper conditions of temperature, the undesirable non-paraffinic hydrocarbons pass into solution to a greater or less extent but a substantial proportion of the desirable paraffinic hydrocarbons remains undissolved. The solution of undesirable hydrocarbons and solvent settles to the bottom of the container and forms an extract phase when relatively heavy solvents are employed. The relatively light paraffinic hydrocarbons rise to the top of the vessel and form a raffinate phase. These phases are then readily separable by ordinary decantation means. The raffinate phase is usually found to contain a small quantity of the selective solvent and the extract phase ordinarily contains a relatively large quantity of the solvent. These fractions may be purified by distillation whereby the solvent is distilled away from the hydrocarbon oils.

In the usual solvent extraction of mineral oil with selective solvents, such as those above mentioned, the separation is not complete. Particularly, all of the paraffinic hydrocarbons, i. e. the more valuable lubricants, are not obtained in the raffinate phase but instead some of the high grade paraffinic oil fractions are found in the extract phase. Due to the similarity of the various hydrocarbon components of mineral oil fractions, such as lubricating oils, the solubility of the undesirable non-paraffinic fractions and the desirable paraffinic fractions in a selective solvent usually differ only in degree and there is, therefore, a tendency for desirable high grade paraffinic oils to be carried away with the extract, resulting in a loss in the yield of paraffinic fractions obtained. In other words, in a phase separation of extract and raffinate fractions from mineral oil by employing a selective solvent, an equilibrium of paraffinic components and non-paraffinic components is established between the phases. Consequently, some of the desirable paraffinic fractions are found in the extract instead in the raffinate.

The solubility of oils of relatively high paraffinicity in the extract phase can be reduced by the

addition of an anti-solvent thereto. An anti-solvent may be defined as a material which tends to prevent the solution of those hydrocarbon fractions which, except for the presence of the anti-solvent, would be dissolved in the extract phase upon extraction of the oil with a selective solvent. The addition of an anti-solvent to the extract phase causes a phase separation between an intermediate raffinate and the remaining extract phase. This intermediate raffinate comprises oil of quality superior to the oil remaining dissolved in the extract phase and it is an object of this invention to return the intermediate raffinate thus rejected to the selective solvent extraction in order that the high quality paraffinic fractions normally lost in the extract phase will be recovered in the final raffinate.

I have found that when oil is countercurrently extracted with a selective solvent and the extract phase therefrom is commingled with an anti-solvent to reject an intermediate raffinate, this intermediate raffinate is characterized by a viscosity gravity constant intermediate that of the raffinate and extract respectively produced by the extraction. It is an object of my invention to aid the rectification of the oil during extraction and to promote the recovery of paraffinic fractions in the raffinate by introducing this rejected raffinate of intermediate quality into the extraction system, preferably into that zone wherein the oil being extracted has substantially similar viscosity gravity constant. The equilibrium of phase distribution in the various zones of the countercurrent extraction is thus undisturbed by the introduction of the intermediate rejected raffinate.

The anti-solvent which I may employ to reject the intermediate raffinate from the extract phase is preferably one which is only partially soluble in the rejected raffinate and is adapted to form a two-phase system with the rejected raffinate and is soluble in the remaining extract phase. Therefore, it is a further object of my invention to extract an oil with a selective solvent to produce raffinate and extract phases and to reject an intermediate raffinate from said extract phase by commingling the latter with an anti-solvent only partially soluble in the rejected raffinate and soluble in the remaining extract phase. The rejected intermediate raffinate is thus relatively free from selective solvent and from anti-solvent and may be directly introduced into that zone of the extraction wherein the oil being extracted has substantially the same viscosity gravity constant as the rejected raffinate being introduced without upsetting the equilibrium of the extraction.

As an anti-solvent having these characteristics, I may employ liquid ammonia, or even water may be used as an anti-solvent when the water forms a solution with the selective solvent with which it is employed. Under certain conditions, the anti-solvent may be a substance which is a selective solvent when employed alone. For instance, there may be mixed with the extract phase to function as an anti-solvent a selective solvent having less solvent power for the higher grade material present therein than the solvent power of the selective solvent originally used to produce the extract. As an example, oil may be treated with chloraniline or a mixture of liquid sulphur dioxide and benzene to obtain an extract phase. These solvents are characterized by high solvent power for higher grade material. To the extract phase thus produced there may be added liquid sulphur dioxide or other solvent having relatively less solvent power for the higher grade material. For this reason and under these conditions, certain selective solvents may be employed as anti-solvents and by their presence in the extract phase the higher grade fractions therein are rejected to form an intermediate raffinate.

In some cases, the addition of an anti-solvent to the extract phase renders temperature reduction unnecessary to separate relatively high quality oil fractions therefrom. In other cases, refrigeration of the extract phase will be necessary but will be less than when no anti-solvent is present. In a solvent extraction process of this character, the expense of refrigeration is a substantial item in the cost of operation. My process lowers this cost.

I have found that when temperature reduction is necessary for rejection and when the anti-solvent employed is a liquid, normally gaseous susbtance such as sulphur dioxide or the like, the rejection of desirable oils from the extract phase by the presence of said anti-solvent is aided when the pressure is sufficiently reduced in the rejection stage to cause evaporation of a portion of the anti-solvent, thereby reducing the temperature of the mixture of the extract phase and anti-solvent remaining liquid. In this case the liquid, normally gaseous anti-solvent also operates as an internal refrigerant. After evaporation for internal refrigeration, sufficient amounts of the liquid normally gaseous anti-solvent should remain in the liquid phase with the extract phase to function as an anti-solvent.

After separation of final raffinate and final extract according to my invention, it is, of course, obvious that these phases may be separated from any solvent and/or anti-solvent associated therewith by distillation or other appropriate means.

The figure is a schematic arrangement of one form of apparatus which may be employed to carry out my process.

Referring to the figure, oil enters the system via line 10 controlled by valve 11 by action of pump 12 and passes into extractor 15 through line 14. It is countercurrently extracted with selective solvent introduced through line 16 controlled by valve 17 by action of pump 18. Raffinate phase from extractor 15 is removed via line 19 controlled by valve 20. Extract phase is removed from extractor 15 by action of pump 21 in line 22 controlled by valve 23.

Extractor 15 is divided into a number of sections 24 to 28 by imperforate plates 29. Each section in turn is divided into a mixing zone 30 and a settling zone 31 by plate 32 provided with port 33. Each mixing zone may be provided with an agitator, if necessary. Phase separation takes place in each settling zone. I prefer to introduce the selective solvent into the uppermost section 24. Raffinate is removed from this section by line 19, while extract phase is removed from the lowest section 28 as described. Extract phase from section 24 is removed therefrom by pump 35 through line 36 controlled by valve 37 and is intermixed with the raffinate phase produced in a lower section of the extractor. This mixture passes through line 38 into the mixing zone 30 of section 25. From this mixing zone the mineral oil mixture and solvent passes through port 33 into settling zone 31. The raffinate from the settling zone of section 25 is removed therefrom by action of pump 40 and passes via line 41 cor

trolled by valve 42 into contact with the solvent entering extractor 15 via line 16.

The extract phases from sections 25 and 26, respectively, are removed by pumps 43 through lines 44 controlled by valves 45 for passage through lines 46 and 47, respectively, into sections 26 and 27, respectively. Raffinate phases from sections 26, 27 and 28, respectively, are removed therefrom by action of pumps 50 in lines 51 controlled by valves 52 for passage through lines 38, 46 and 47, respectively, into sections 25, 26 and 27, respectively. Thus, the raffinate phase from a lower section is commingled with an extract phase from an upper section and the mixture is extracted in an intermediate section. Extract phase from section 27 is forced by action of pump 53 through line 54 controlled by valve 55 into section 28 via line 14 in intermixture with oil freshly introduced into extractor 15.

An anti-solvent passing through line 60 controlled by valve 61 by action of pump 62 is commingled with the extract phase exiting from extractor 15. As previously stated, this extract phase comprises relatively paraffinic hydrocarbons which are desirable in the final raffinate issuing via line 19. This mixture of extract phase and anti-solvent passes through line 63 into cooler 64 for the rejection of the intermediate grade raffinate from the extract phase. In some cases, cooler 64 may be omitted in which event the intermediate raffinate will be rejected from the extract phase without temperature reduction. Cooling in 64 may be accomplished by external means, or if the selective solvent and/or the anti-solvent is normally gaseous, cooling may be by the internal refrigeration above described. The extract phase and anti-solvent then passes through line 65 into separator 66 wherein rejected intermediate raffinate is removed. Extract phase passes from separator 66 via line 67 controlled by valve 68.

As previously stated, the rejected intermediate raffinate separated from the extract phase in 66 is characterized by a viscosity gravtiy constant intermediate that of the final raffinate issuing from extractor 15 via line 19 and that of the extract phase passing from extractor 15 via line 22 and some of the fractions contained therewith are desired in the final raffinate. I prefer to introduce the rejected intermediate raffinate into the extraction at a point intermediate the points of introduction of selective solvent and of oil entering the system. Otherwise stated, the rejected intermediate raffinate may be introduced into the extraction at a point intermediate the point of introduction of oil entering the system and the point of removal of raffinate from said extraction. Preferably, I return the rejected intermediate raffinate into that portion of extractor 15 wherein the oil being extracted has substantially the same viscosity gravity constant as the rejected raffinate being introduced. In order to accomplish this, the rejected intermediate raffinate passes by action of pump 70 through line 71 controlled by valve 72. In order for the rejected intermediate raffinate to enter section 25, it is passed via line 73 and valve 74 into line 38. In order to introduce rejected intermediate raffinate into section 26, it passes via line 75 and valve 76 into line 46. The rejected intermediate raffinate can be passed into section 27 via line 73 and valve 77 into line 47. To pass rejected intermediate raffinate into section 28 it may travel through line 75 and valve 76 into line 14.

In order to exemplify the application of my invention in the above described apparatus, oil characterized by viscosity gravity constant of 0.875 may be introduced into extractor 15 via lines 18 and 14. This oil may be selectively extracted with 300 volume percent. phenol introduced via line 16. Final raffinate issuing via line 19 may have a viscosity gravity constant of 0.810. The extract passing from extractor 15 through line 22 may be characterized by a viscosity gravity constant of 0.890. To this extract may be added an anti-solvent such as water to the amount of 20 volume percent. based upon the quantity of oil entering the extractor via line 18. Low grade extract with a viscosity gravity constant of 0.940 issues from separator 66 via line 67. Rejected intermediate raffinate with a viscosity gravity constant of 0.835 is returned to the extractor, in the manner above described, into that zone wherein oil of substantially the same viscosity gravity constant is being extracted, for instance, section 26.

As another example of the operation of my invention, oil characterized by a viscosity gravity constant of 0.840 may be introduced into extractor 15 for selective extraction with 200 volume percent. of a mixture comprising 140 volume percent. liquid sulphur dioxide and 60 volume percent. benzene. The raffinate passing through line 19 is characterized by a viscosity gravity constant of 0.806 and the extract phase with a viscosity gravity constant of 0.860 passing through line 22 is intermingled with 300 volume percent. liquid sulphur dioxide to reject an intermediate raffinate characterized by a viscosity gravity constant of 0.828. This intermediate raffinate is returned to that zone of extractor 15 wherein the oil being extracted has substantially the same viscosity gravity constant, for instance, section 25.

It is obvious that many modifications of my invention may be made, for instance, the low grade extract phase passing through line 67 may be employed as a selective solvent in another solvent extraction and the raffinate produced therein may be used as the incoming oil passing to extractor 15 via lines 18 and 14. As a further modification, the oil introduced into my extraction system may be primarily deasphaltized by commingling with an asphalt precipitant such as liquid ethane, propane, butane or the like, and after removal of the asphalt, the oil and asphalt precipitant may pass into extractor 15 via lines 18 and 14 for the above described treatment therein.

As another modification, if the rejected intermediate raffinate is associated in solution with anti-solvent and/or above described asphalt precipitant, this mixture may be heated to vaporize the anti-solvent and/or asphalt precipitant before the rejected intermediate raffinate is returned to the extraction into that zone wherein oil of substantially the same viscosity gravity constant is being extracted. In this case after removal of these materials, it is preferred to cool the heated rejected intermediate raffinate to the temperature prevailing in the extractor before its introduction therein. The equilibrium of phase distribution in the extraction is then maintained. If desired, orifice mixers may be placed in lines 16, 38, 46, 47 and 14 in order to secure thorough inter-mixture of the various materials passing into the respective sections of the extractor. Also, extractor 15 may be divided into more or fewer sections. Or in fact, it may be undivided into

sections in which case the oil and solvent can freely flow up and down the column.

It is to be understood that the foregoing is merely illustrative of the generic invention and the examples are not to be taken as limiting thereof as many modifications of my invention may be made within the scope of the following claims:

1. A process for the separation of oil into paraffinic and non-paraffinic fractions which comprises, commingling said oil with a selective solvent and thereby forming a raffinate phase containing paraffinic oil fractions and an extract phase containing selective solvent and dissolved oil fractions, separating said phases, commingling said extract phase with an anti-solvent, said anti-solvent being more soluble in the extract phase than in the raffinate phase and adapted to cause separation of the extract phase into two layers, one layer containing oil fractions relatively more paraffinic in character than the other of said layers, separating said layers and returning the more paraffinic oil layer to the extraction system, at a point between the points of introduction of the oil and selective solvent into said system.

2. A method as claimed in claim 1 in which the selective solvent is sulphur dioxide mixed with benzol and the anti-solvent is sulphur dioxide.

3. A process for the separation of oil into paraffinic and non-paraffinic fractions which comprises, commingling said oil with a selective solvent and thereby forming a raffinate phase containing paraffinic oil fractions and an extract phase containing selective solvent and dissolved oil fractions, separating said phases, commingling said extract phase with an anti-solvent, said anti-solvent being more soluble in the extract phase than in the raffinate phase and adapted to cause separation of the extract phase into two layers, one layer containing oil fractions relatively more paraffinic in character than the other of said layers, separating said layers and returning the more paraffinic oil layer to that zone of the extraction system wherein the oil being extracted has substantially the same viscosity-gravity constant as the oil returned to said extraction system.

4. A process for the separation of oil into paraffinic and non-paraffinic fractions which comprises countercurrently extracting said oil with a selective solvent and thereby forming a raffinate phase containing paraffinic oil fractions and an extract phase containing selective solvent and dissolved fractions, separating said phases, commingling said extract phase with an anti-solvent, said anti-solvent being more soluble in the extract phase than in the raffinate phase and adapted to cause separation of the extract phase into two layers, one layer containing oil fractions relatively more paraffinic in character than the other of said layers, separating said layers and returning the more paraffinic oil layer to the countercurrent extraction system at a point intermediate the points of introduction of the oil and selective solvent into said system.

5. A process according to claim 4 in which the point of return to the extraction system of the oil layer recovered from the extract phase is that point at which the viscosity gravity constant of the oil undergoing extraction is substantially the same as the viscosity gravity constant of the oil layer recovered from the extract phase.

6. A process according to claim 1 in which the extract phase containing the anti-solvent is cooled prior to separation of the extract phase into layers.

7. A process according to claim 4 in which the extract phase containing the anti-solvent is cooled prior to separation of the extract phase into layers.

8. A process according to claim 4 in which the more paraffinic oil layer recovered from the extract phase is freed from its selective solvent content and anti-solvent content prior to its return to the extraction system.

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