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SOLVENT RECTIFICATION OF PETROLEUM

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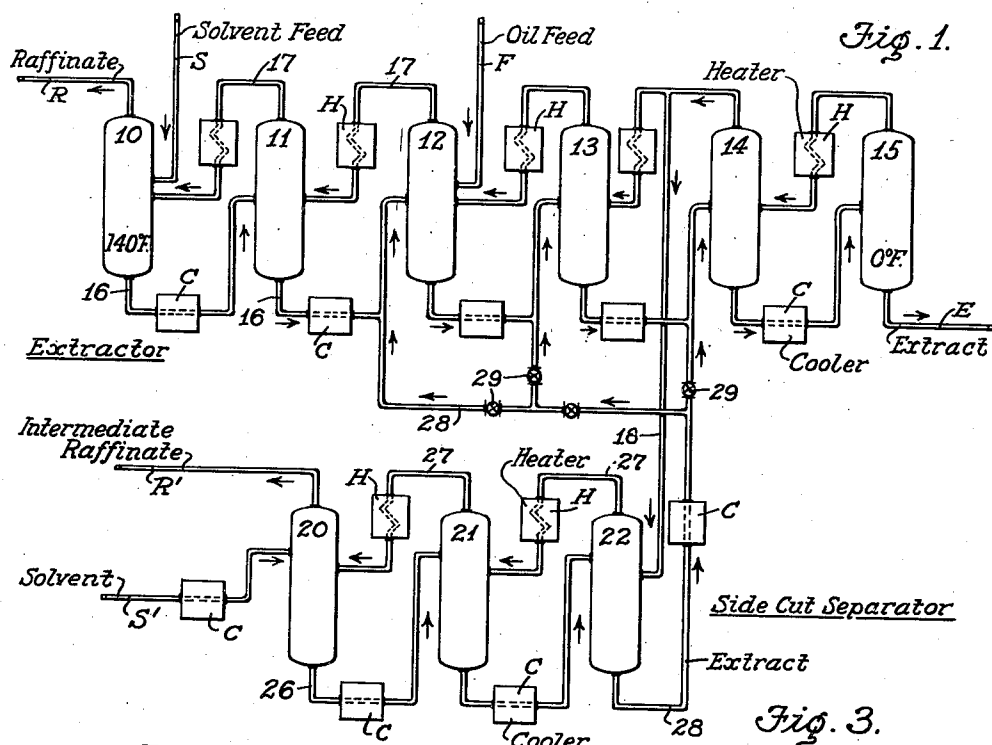
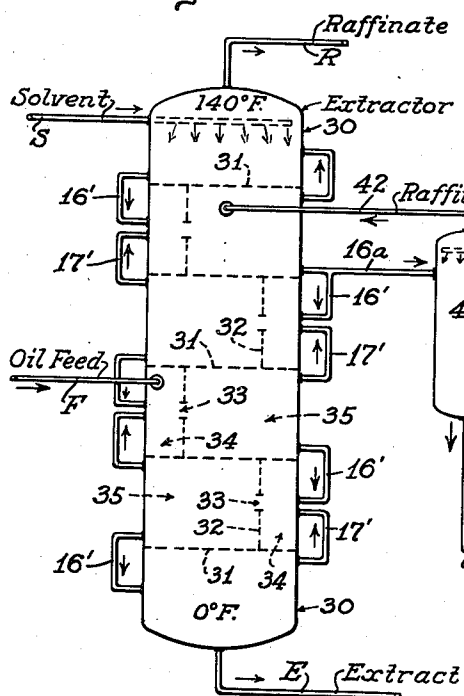
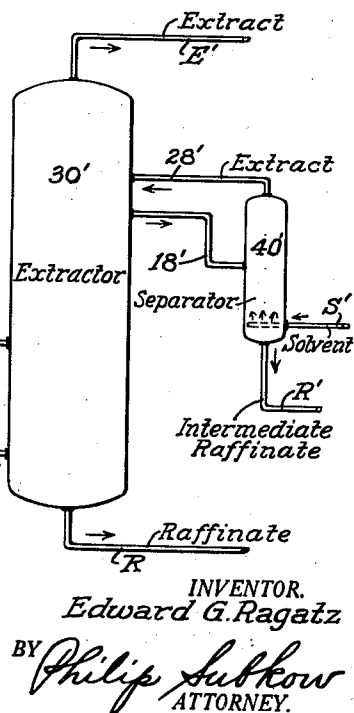


Fig. 2.



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SOLVENT RECTIFICATION OF PETROLEUM

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21 Claims. (Cl. 196—13)

This invention relates to the refining of petroleum oils by the solvent extraction method, particularly to the preparation of petroleum lubricating oils by the employment of selective solvents for the removal in the solvent of constituents such as aromatics which are not desired in the lubricant, and naphthenics which also are undesirable.

Solvent extraction of this character is commonly carried on with solvents in the liquid phase, such as acetone, cresol, sulfur dioxide, aniline, furfural, dichlorethyl ether, nitrobenzene, chloraniline, and the like, or various mixtures of these or mixtures such as sulfur dioxide and benzol, and the like, known to the art.

The present invention relates particularly to treatment of the stock with such solvents as above indicated by means of the countercurrent method of treatment, wherein the feed may be introduced at an intermediate point, the raffinate withdrawn from one end of the system and the extract from the other.

The object of the present invention is to improve the rectification and separation of the raffinate and extract cuts and also to provide for the recovery of an intermediate raffinate cut or an intermediate extract cut if desired.

The feature of the present invention resides in withdrawing from an intermediate point in the system a side cut, which may be either of the raffinate phase or the extract phase, and separately treating this side cut to obtain an intermediate cut, the necessary temperature gradient for proper separation being maintained in the system. Where an intermediate raffinate cut is desired, the removed side cut is separately treated to obtain phase separation, the raffinate being recovered as the desired intermediate cut and the extract preferably being returned to the countercurrent system for further rectification therein and final removal. The intermediate product so obtained may be removed by the present method. Thus not only is provision made for obtaining a quantity of one phase of the side cut as an intermediate product when desired, but the return of the other phase results in bypassing a portion of the materials in the system in order to obtain a desired balance therein for various operating conditions when necessary or desirable. The return of the extract to the system causes the extract to act as a wash oil thereby further fortifying the succeeding rectification steps in the separation of the raffinate from the extract, and the separate treatment of the side cut in conjunction with return of its extract also

serves to change the distribution ratio and to result in the effective rejection of more of the paraffinic constituents from the system at and beyond the point of withdrawal of the intermediate cut than would be the case if no subdivision of the stream had been effected. This is obvious when it is considered that return of the intermediate extract minus its raffinate serves further to dilute the paraffinic materials passing toward the end of the system from which the extract is removed.

Similarly, if an intermediate extract be desired, the raffinate phase therefrom may be returned to the system. The process is particularly useful with two types of solvents; first, those which are good solvents for the extract to be removed but not thorough anti-solvents for the raffinate to be separated, and second, those that are thorough anti-solvents for the raffinate but not thorough solvents for the extracts to be rejected. In the first instance the extract contains raffinate which is best rejected from the extract by treatment of side cut taken preferably from the extract-discharge end of the system beyond the oil feed. In the second instance the raffinate contains extract which is best rejected by treatment of a side cut preferably taken from between the oil feed and the raffinate discharge.

The invention, therefore, may be further stated as comprising removing a side cut in a solvent treating process, separating the side cut into its phases, and returning one of the phases to the primary treating system for modifying the distribution ratio therein to insure adequate separation and effective rejection of each phase from the others.

Certain embodiments of the invention are disclosed by way of illustration in the accompanying drawing, wherein—

Figure 1 is a diagrammatic arrangement of the solvent treating system for petroleum oils employing separate chambers for each stage of operation, a side cut being withdrawn and separated in the series of chambers;

Figure 2 illustrates a conventional rectification type of column from which a side cut is removed at an intermediate point and treated in another column to effect separation; and

Figure 3 illustrates diagrammatically a column type of apparatus similar to that of Figure 2, the solvent employed being lighter than the oil being extracted.

According to the embodiment of Figure 1, the extraction process is carried on in a series of extracting chambers 10, 11, 12, 13, 14 and 15

through which oil and solvent pass, separation in each chamber being effected by gravity, the various liquids being passed from chamber to chamber through the medium of pumps (not shown) as may be required. The oil to be treated is introduced into an intermediate chamber such as chamber 12 by way of the oil feed line F, the solvent employed, which may be any one of those heretofore mentioned, is preferably introduced into the upper portion of the first chamber 10 of the series through the solvent feed line S. The treated or finished oil is removed from the upper portion of the chamber 10 by way of the raffinate discharge line R. According to this form of the invention as here illustrated the solvent employed is heavier than the oil to be treated, and in each chamber moves countercurrently downward in temporary contact with the oil, gradually separating therefrom and being discharged from the respective chamber through an extract conduit 16. Preferably the extract which is removed from the bottom of each chamber is introduced into the next chamber at an intermediate point. The raffinate phase separated in each chamber is removed from the top thereof and conducted by the raffinate line 17 to an intermediate portion of the preceding chamber. Any suitable provision may be made for mixing the extract and raffinate phases being introduced into each chamber; as illustrated the streams are directed toward each other in opposed relation, but it is obvious that both might be introduced through a common discharge nipple if desired, the present showing being made for purposes of simplification. The final extract from the last chamber 15 of the series is removed by way of the final extract line E. In practice it probably will be desirable to maintain a temperature gradient throughout the system, the highest temperature being maintained in the solvent feed chamber 10 and the lowest temperature being maintained in the extract discharge chamber 15. For example, a temperature of about 140° F. may be maintained in chamber 10 and a temperature of about 0° F. in chamber 15, a corresponding gradient existing in the intermediate chambers. Such cooling as may be required of the extract passing from one chamber to the next may be effected by the coolers C and such heating of the raffinate phases as may be necessary may be effected in the heaters H. Obviously any heat interchange means may be employed for these purposes such as heat interchange between the extract and raffinate phases themselves.

It is the purpose of the present invention to withdraw an intermediate or side cut from the system and treat the same for separation thereof into desired raffinate and extract phases. According to Figure 1 it is desired to obtain an intermediate raffinate product, and to return the corresponding intermediate extract phase to the system for dilution in the portion of the system near the extract discharge in order to insure adequate rejection of the paraffinic material from the extract. Ordinarily a situation of this kind will arise wherein the solvent is especially selective for the extract, the result being a carrying over of an undesired quantity of raffinate to the extract. According to this form, a raffinate phase is withdrawn from a point in the system intermediate the oil feed F and the extract discharge E. The drawing particularly illustrates the splitting of the raffinate phase being discharged from the top of the chamber 14, part of this phase continuing on through the system

by way of the line 17, and the other part being withdrawn through the line 18 and conducted away from the primary system above described to a secondary system which constitutes a side cut separator and comprises a second series of treating chambers 20, 21 and 22. This split stream of a raffinate phase is introduced into an intermediate portion of the chamber 22 for treatment therein. The raffinate phase separating in the chambers 21 and 22 is carried forward to the preceding chamber through raffinate lines 27, and the raffinate separating in the chamber 20 is recovered as an intermediate raffinate product discharged through the line R'. In order to effect adequate separation of the side cut being treated in the chambers 20, 21 and 22, it may be necessary to introduce additional solvent into the chamber 20, and this will be effected through the line S'. The extract phase separating in each of the chambers 20 and 21 will be passed to the next chamber through the extract lines 26 and discharged in such manner as to mingle readily with the raffinate phases being introduced into the respective chambers. This applies also to the introduction of the solvent through line S' in chamber 20, in each case effected either by introduction of the solvent or extract directly opposite to the raffinate or to a point above the raffinate introduction or by introduction through a common discharge nipple (not shown). The extract phase taken from the bottom of the chamber 22 of the secondary system or side cut separator unit is returned to the primary extractor system through the line 28 and may be discharged into any one of the chambers 12, 13, and 14, this being controlled by means of the valves 29 inserted in the various branches of line 28. The point of such return of extract will be determined by the dilution of the paraffinic phases with the extract required in the stages adjacent the extract discharge.

In the manner above described it is possible to obtain the desired intermediate raffinate, and at the same time remove entirely from the final extract all paraffinic fractions which are desired in the primary raffinate recovered through line R, this desired sharp separation being insured by the dilution of the extract as herein described.

Figure 2 illustrates diagrammatically an apparatus of the rectification column type, wherein separations may be obtained analogous to those resulting from the use of the apparatus and process of Figure 1. Here there is illustrated the treatment of the side cut to obtain an intermediate extract product, the resultant intermediate raffinate being returned to the primary system. In this instance the column 30 is divided into a plurality of horizontal zones by means of horizontal partitions 31. Each of these zones may in turn be divided by vertical partitions 32 apertured at 33 and forming mixing chambers 34 and settling or separating chambers 35. As in the case of Figure 1, solvent is fed into the upper zone through a solvent feed line S and the final raffinate product is recovered from the upper zone through raffinate line R. Oil to be treated is fed to an intermediate zone through an oil feed line F, and extract is removed from the bottom through extract discharge line E. Extract phases from each zone are led to an intermediate portion of the next lower zone through extract conduits 16' and raffinate phases are fed from one zone to that one next above through raffinate conduits 17'. In order to remove from the raffinate discharge end of the system quan-

titles of extract which may be carried there-through by the solvent, and also in order to recover an intermediate extract cut if desired, the extract phase leaving one of the upper zones is divided, only a portion thereof being continued downward through the system and the other portion carried through the line 16a to the extractor column 40.

Column 40 serves as a secondary or separator system wherein the divided side-cut drawn from extractor column 30 through the line 16a is in turn separated into raffinate and extract phases. Separation is caused to take place in separator 40 through the agency of gravity, and may be facilitated if necessary by zone divisions as in column 30, or by maintenance of such temperature gradients as may be desired, or by introduction of additional solvent through the line S' the solvent being cooled in cooler C if necessary, or by any combination of these or other means. Of course the cold solvent introduced through the line S' should be in quantity small enough not to overcome the beneficial effects of the cooling produced thereby. The resultant intermediate extract is withdrawn from the bottom of separator 40 through line 41, and the resultant raffinate separating in the top of separator 40 is returned to the system through the line 42. Preferably the raffinate return is made at a point in the vicinity of the withdrawal of the side-cut, although such other point of return may be employed as may be necessary or desirable. The return of the raffinate to the upper portion of column 30 results in a change of the distribution ratio between the raffinate and the extract phase and insures a more complete and effective rejection of the extract from the raffinate so that a clean raffinate may be recovered from the line R. In both of the columns 30 and 40 any desired temperature gradient may be maintained, and normally will be maintained. For example, the range in column 30 may lie between 140° F. in the upper part of the column and 0° F. at the bottom, the temperatures in the separator 40 varying between these limits. Obviously temperatures will be varied and regulated to meet the separator requirements in each particular instance.

In Fig. 3 there is illustrated diagrammatically the arrangement of feed and discharge in a system wherein the extract is lighter than the oil being treated, thereby distinguishing from the systems illustrated in Figs. 1 and 2. In this instance the oil feed F is made near the middle of the extractor column 30', the solvent feed S is to the lower end thereof, the raffinate-discharge R leads from the bottom and the extract-discharge E' leads from the top. The side-cut taken off through line 18' is being treated for the recovery of an intermediate raffinate and is withdrawn from a point between the oil feed F and the extract-discharge E'. The treatment of this raffinate side-cut is effected in separator 40', to the bottom of which additional solvent may be fed through the line S', the intermediate raffinate product (corresponding to that recovered from the line R' of Fig. 1) being withdrawn from the bottom of separator 40' by way of line R'. The extract separating in separator 40' is returned to column 30' through the line 28' in a manner similar to the return of extract from the auxiliary system of Fig. 1 through the line 28 to the primary system of Fig. 1.

From the foregoing it will be apparent that the application of the removal and separation of

side-cuts for the sharper fractionation of the two phases in solvent extraction, as well as for the recovery of an intermediate product, may be used where the solvent is either lighter or heavier than the oil being treated, and may be employed to treat either an intermediate extract phase or an intermediate raffinate phase to obtain sharper cuts by variation in the distribution ratio of either phase in the vicinity of the take off or return of the side-cut, or both, and may be employed likewise for the recovery of either an intermediate raffinate product or an intermediate extract product. The side-cut may of course be withdrawn from any intermediate point of the primary systems illustrated, and then separated for the return to any point of the primary system of any such phase division as may be necessary or desirable. By such arrangement of withdrawal and return any desired character of intermediate product or any desired character of change in distribution ratio of the phases within the extracting systems may be made at will. Ordinarily the return of the diluting phase to the column will be made at approximately the point of withdrawal of the original side-cut, and ordinarily such phase will be returned to the primary system at a point farther along in the direction in which that phase was moved at the time of its withdrawal; this also however may be varied as required. Thus the withdrawal of intermediate side-cuts, their separation and the return to the primary system of one of the phases may be relied upon to effect the desired sharp separation required in any ordinary solvent extracting system, and correction will thereby be effected to compensate for any solvent preference for the raffinate or insufficient solvent action for the extract. Likewise this system of rectification in solvent extraction may be relied upon to correct for different results under different temperature gradients with the same solvent; for instance, in those cases where a solvent, such as liquid sulphur dioxide, has greater affinity for the raffinate at certain temperatures, and under other temperature conditions has insufficient solvent preference for the extract to insure thorough separation in a normal system. The ability of the present process to modify the distribution ratio between the extract and raffinate phases at either end of the system according to a solvent's characteristics, thereby to effect sharp separation between the final extract and the final raffinate, is an outstanding feature of the present invention.

Ordinarily the feed oil to be treated either should have been previously dewaxed to avoid interference by precipitation of the wax at lower temperatures, or provision should be made for removal of such wax after precipitation in the present systems. In maintaining a temperature gradient in the secondary or separator system, the temperatures in general will approximate those of the corresponding zones in the primary system. Thus in Fig. 1, the temperatures in chambers 20, 21 and 22 might graduate from 90° F. in 20 down to about 20° F. in 22, as compared with similar temperature in chambers 12, 13 and 14. In making return of the side cut phase to the primary system at a point near the original withdrawal of the side cut, a slight or substantial advance of the return point beyond the withdrawal point in the direction in which the returned phase was originally moving will sometimes be an aid to better phase separation in the rest of the system.

It is to be understood that the disclosures here made are to be construed as merely illustrative of the generic invention and not as limiting.

The present process is applicable for treatment of all oils containing aromatic and/or naphthenic compounds, such as California, Mid-continent and other petroleum, for separating said compounds and other undesired constituents in a solvent extract. The aromatic and naphthenic compounds present in crude lubricating oil fractions are undesirable because of their high temperature viscosity susceptibility. These compounds exhibit too great a change in viscosity for a given change in temperature. The paraffinic hydrocarbons present in crude lubricating oil fractions are the most desirable materials to be employed as lubricants. These compounds are highly saturated. Hence, from a chemical standpoint, they are rather inactive and do not exhibit a tendency towards the formation of undesirable resinous or sludge forming constituents. Furthermore, these paraffinic compounds exhibit a low temperature viscosity susceptibility. In other words, they exhibit a minimum change in viscosity for given change in temperature. Also they are stable to sunlight, exhibiting low oxidation value and do not have a tendency towards the formation of sludge forming constituents. The term "paraffinic hydrocarbons" is used to mean those compounds present in petroleum having the aforementioned characteristics and liquid at ordinary temperatures. This group does not include those compounds present which are usually solid or semi-solid at ordinary temperature known as "wax" or "paraffins."

I claim:

1. A process for refining oils comprising treating an oil countercurrently in a system with a selective solvent adapted to remove as an extract constituents undesired in the oil and to yield raffinate and extract phases, dividing out and withdrawing from an intermediate part of the system an intermediate cut less than all of the corresponding material while continuing through the system the remaining materials, separately treating said intermediate cut to produce an intermediate raffinate phase and an intermediate extract phase, separating said intermediate phases and returning one of the phases to the countercurrent system to change the distribution ratio between the two phases and facilitate phase separation.

2. A process for the refining of petroleum oils comprising treating the oils countercurrently in a plurality of stages with a selective solvent adapted to remove in the extract constituents undesired in the oil and to yield a raffinate phase and an extract phase, withdrawing at an intermediate stage an intermediate cut as a part of one of the phases while continuing the remaining portion of that phase through the system, separately treating the intermediate cut so withdrawn apart from the feed-oil supply to produce a raffinate phase and an extract, separately removing one of the last mentioned phases and returning the other to the countercurrent system.

3. A process for the solvent refining of petroleum oils comprising passing a petroleum oil and a liquid which is a selective solvent for constituents undesired in the oil, in countercurrent relation through a plurality of stages, to produce raffinate phases and extract phases, recovering a raffinate phase from one end of the system and an extract phase from the other end of the sys-

tem, dividing a phase from an intermediate stage in the system, continuing one portion of the divided phase through the system, withdrawing the other portion and separately treating the latter to yield an intermediate raffinate phase and an intermediate extract phase, separately recovering one of the intermediate phases as an intermediate product, and returning the other intermediate phase to the countercurrent system.

4. A method according to claim 2 wherein a temperature gradient is maintained ranging downward from the raffinate-discharge end of the system to the extract discharge.

5. A method according to claim 3 wherein a temperature gradient is maintained ranging downward from the raffinate discharge end of the system to the extract discharge.

6. A process for the solvent refining of petroleum oils comprising passing a petroleum oil in countercurrent relation with a liquid which is a selective solvent for constituents undesired in the oil to produce raffinate phases and extract phases, removing a final raffinate phase from one end of the system and a final extract phase from the other end of the system, dividing an intermediate phase from an intermediate zone in the system, continuing one portion of the divided phase through the system, withdrawing the other portion of the divided phase and separately treating the latter to yield intermediate raffinate and extract phases, separately recovering the intermediate raffinate phase as an intermediate raffinate product, and returning the intermediate extract phase to the countercurrent system.

7. A method according to claim 6 wherein the intermediate phase is a raffinate phase withdrawn from the countercurrent system at a point between the oil feed to the system and the final extract-discharge from the system.

8. A method according to claim 6 wherein the intermediate phase is withdrawn from the countercurrent system at a point between the oil feed to the system and the final extract discharge from the system, a temperature gradient being maintained in the primary system ranging downward from the raffinate discharge toward the extract discharge.

9. A process for the solvent separation of petroleum into raffinate and extract phases, comprising treating the petroleum with a selective solvent for constituents desired in one of the phases by contacting the petroleum and the solvent to cause the two phases to pass countercurrently through a primary system in a plurality of stages, removing the raffinate phase from one end of the system and the extract phase from the other end, dividing one of the phases at an intermediate point in the system, continuing one portion of the divided phase through the system, removing the other portion as a side cut and separately treating the latter in an auxiliary system to yield an intermediate extract phase and an intermediate raffinate phase, and returning one of the intermediate phases to the primary system for further treatment.

10. A method according to claim 9 wherein the solvent employed is a good selector as to the extract phase and at the same time tends to take raffinate into the extract phase, and the extract phase of the side cut is returned to the primary system.

11. A method according to claim 9 wherein the solvent employed is a good anti-solvent as to the raffinate phase and at the same time tends to permit extract in the raffinate phase and the

raffinate phase of the side cut is returned to the primary system.

12. A process for the separation of a petroleum fraction into a raffinate phase and an extract phase comprising treating the petroleum fraction with a solvent which is a good selector for constituents not desired in the raffinate phase and which tends to take raffinate into the extract phase, passing the petroleum and the solvent in countercurrent relation through a plurality of stages in a primary system, introducing the petroleum fraction into an intermediate stage of the system, causing the mixed materials to separate into raffinate and extract phases throughout the system, removing the final raffinate and from one end of the system and a final extract from the other end of the system, separating an intermediate raffinate phase at a stage intermediate the petroleum feed and the extract discharge, dividing said intermediate phase, continuing one portion thereof through the system, removing the other portion as a side cut and separately treating the latter in an auxiliary system to yield an intermediate extract phase and an intermediate raffinate phase, separately recovering said intermediate raffinate phase and returning the intermediate extract phase to an intermediate stage of the primary system.

13. A process for the solvent separation of a petroleum fraction into a raffinate phase and an extract phase, comprising contacting said fraction with a solvent for constituents not desired in the raffinate, said solvent being a good antisolvent as to the raffinate but at the same time tending to leave desired extract in the raffinate phase, passing the mixture in countercurrent relationship through a plurality of stages in a primary treating system, introducing the petroleum fraction at an intermediate stage of the system, removing the final raffinate from one end of the system and the final extract from the other end, separating an intermediate extract phase at an intermediate stage of the system between the feed and the raffinate discharge, dividing said intermediate phase, continuing one portion thereof through the system, withdrawing the other portion as a side cut, separately treating the latter in an auxiliary system to yield an intermediate extract phase and an intermediate raffinate phase, separating the intermediate raffinate phase and returning the raffinate phase to an intermediate stage of the primary system.

14. A method according to claim 12 wherein the intermediate extract phase is returned to a stage of the primary system adjacent that from which the side cut was withdrawn.

15. A method according to claim 13 wherein the intermediate raffinate phase is returned to the primary system at a stage adjacent that from which the side cut was withdrawn.

16. A method according to claim 12 wherein a temperature gradient is maintained ranging downward from the raffinate discharge to the extract discharge.

17. A method according to claim 13 wherein a temperature gradient is maintained ranging downward from the raffinate discharge to the extract discharge.

18. A process for refining petroleum oils comprising primarily treating the oils in a plurality of stages with a solvent for aromatic and naphthenic constituents to yield a solvent extract phase and a raffinate phase, withdrawing an intermediate cut from an intermediate stage, continuing the remaining materials from which the cut is taken through the system, separately treating said cut to produce an intermediate raffinate phase free from aromatic and naphthenic constituents and to produce an intermediate solvent extract phase including such constituents, separating said intermediate phases and returning one of said intermediate phases to the primary treatment.

19. A process according to claim 18 wherein the returned phase is returned to the primary treat toward that end of the treatment in which the like phase is traveling.

20. A process for refining oils comprising treating an oil countercurrently in a system with a selective solvent adapted to remove as an extract constituents undesired in the oil and to yield raffinate and extract phases, feeding the oil into an intermediate portion of the system, withdrawing from another intermediate portion of the system an intermediate cut less than all the corresponding material while continuing the remaining corresponding material through the system, separately treating said withdrawn intermediate cut apart from the feed-oil supply in conjunction with cooling thereof to produce an intermediate raffinate phase and an intermediate extract phase, separating said intermediate phases and returning one of the phases to the countercurrent system to change the distribution ratio between the two phases and facilitate phase separation.

21. A process according to claim 3 wherein the withdrawn portion of the divided intermediate phase is withdrawn from a point in the system between the point of oil feed and the point of selective solvent feed.

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