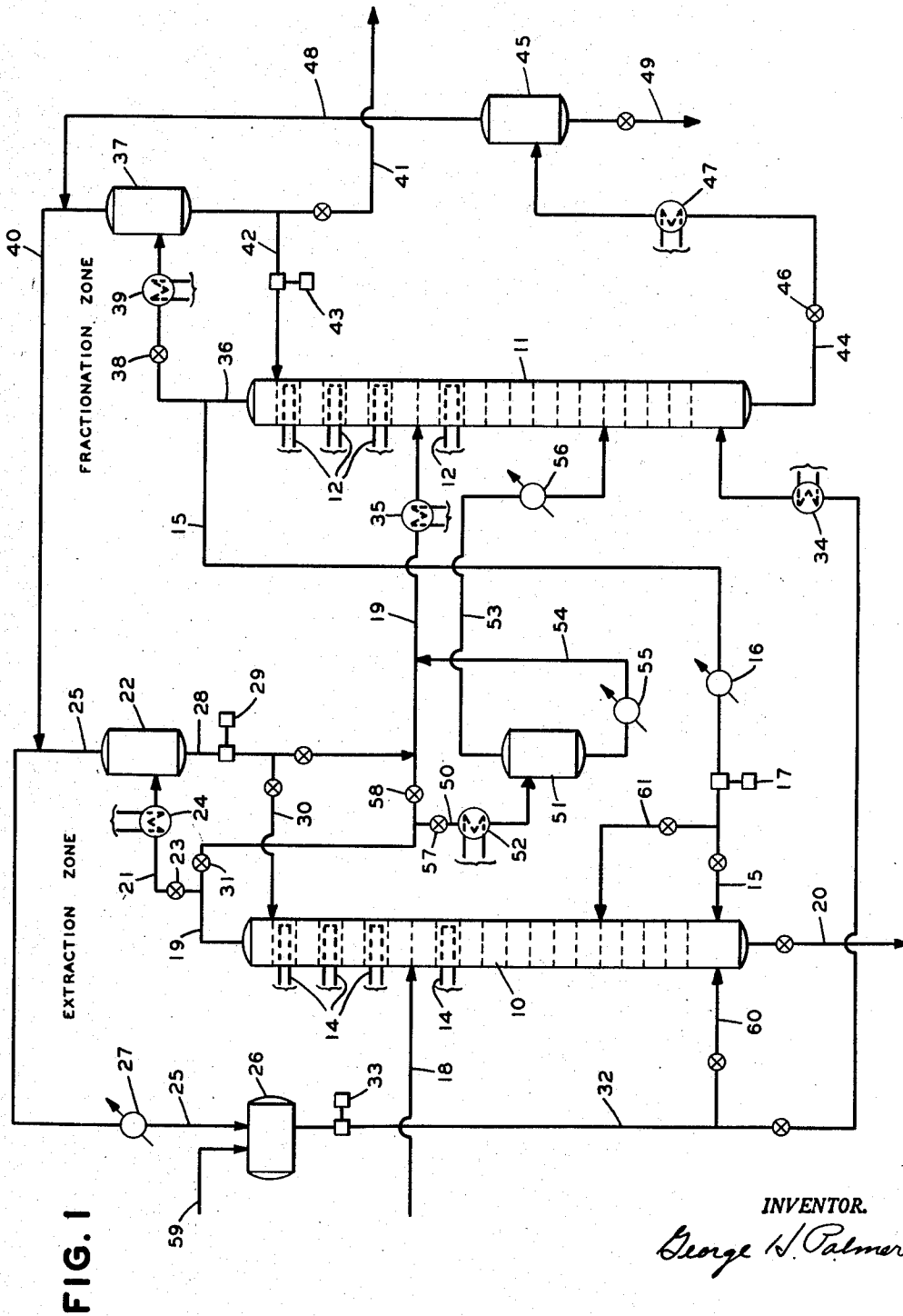


Filed Feb. 5, 1948

REFINING FATTY OILS

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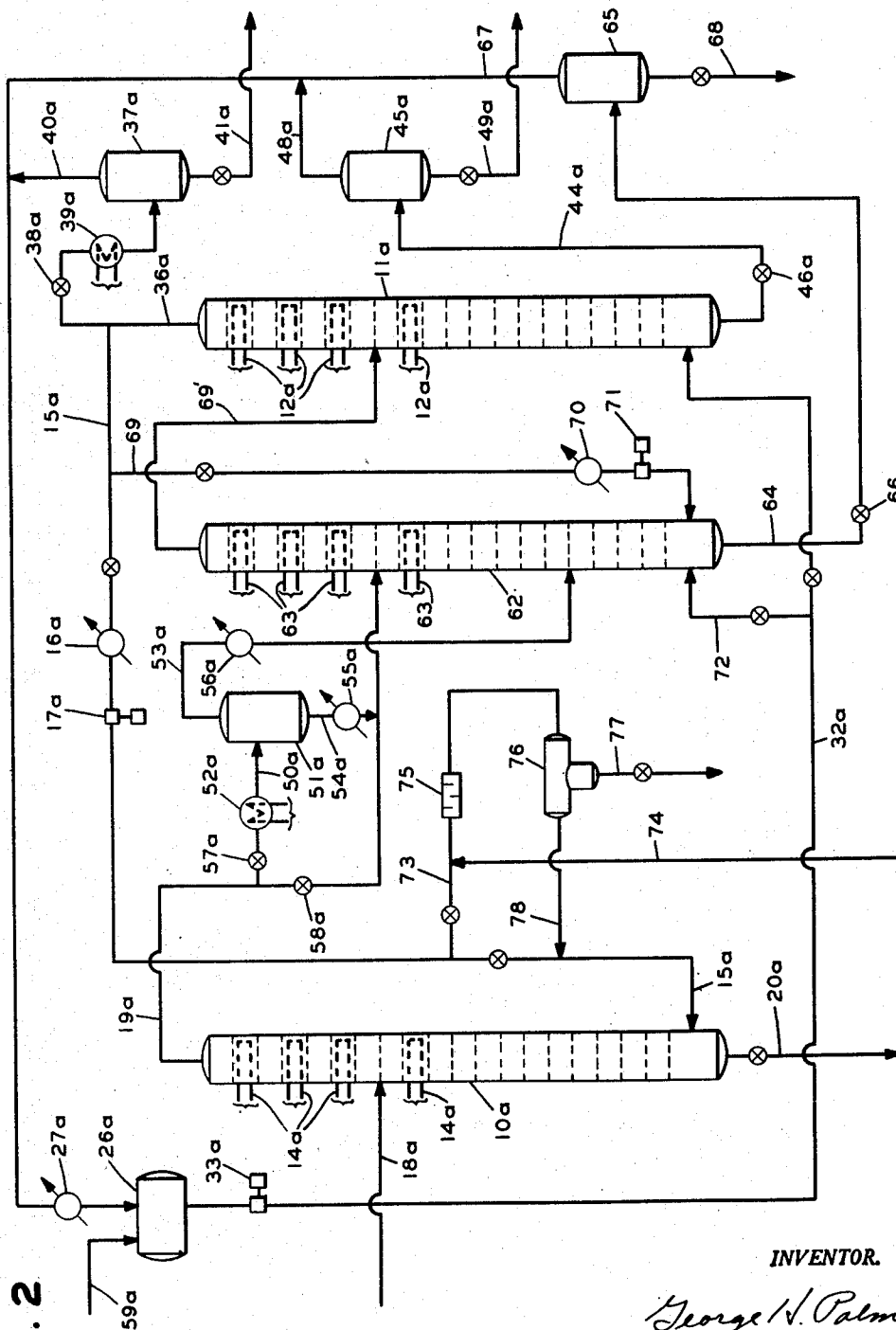
April 25, 1950

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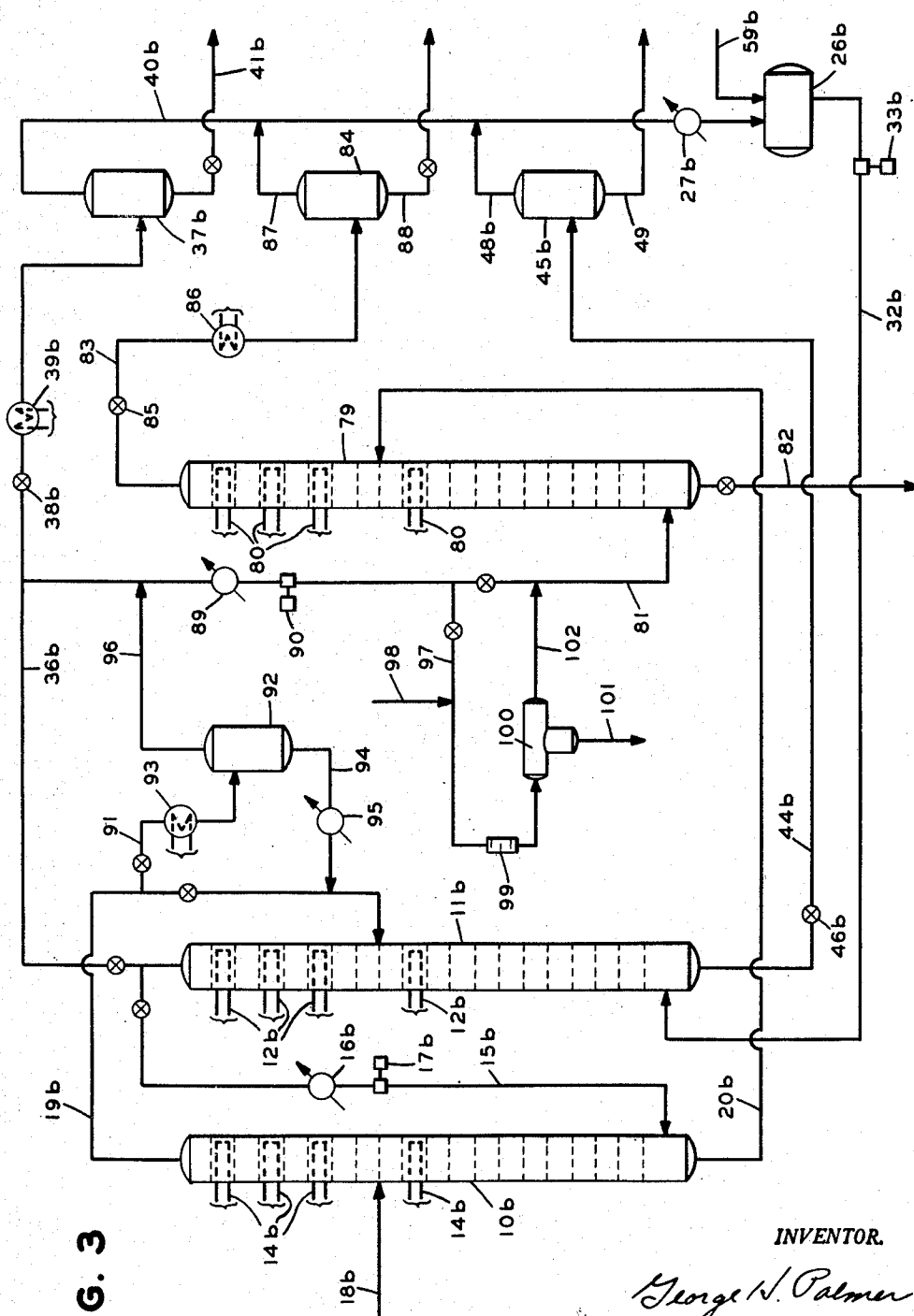
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UNITED STATES PATENT OFFICE

2,505,338

REFINING FATTY OILS

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Application February 5, 1948, Serial No. 6,459

16 Claims. (Cl. 260—428.5)

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This invention relates to improvements in the refining and fractionation of fatty oils, i. e. oils consisting principally of glycerol esters of fatty acids, such as cottonseed oil, cocoanut oil, linseed oil, soybean oil, palm oil, peanut oil, sardine body oil, cod liver oil, menhaden oil, and whale oil.

It has been suggested previously to fractionate fatty oils by contacting the oil with a low-boiling solvent at temperatures in a temperature range, near the critical temperature of the solvent, in which the solubility of the oil and solvent decreases with rising temperature. This temperature range lies above the temperature of maximum solubility which is ordinarily not more than about 100° F. below the critical temperature of the solvent, and extends to a few degrees above the critical temperature of the solvent.

In this temperature range solubility is greatly affected by conditions which affect the density of the solvent. The condition of the solvent in this temperature range, in which its solvent power is greatly affected by slight changes in temperature and/or pressure, has been designated arbitrarily as the "paracritical state." In this condition the pressure is always maintained sufficiently high to keep the solvent substantially entirely in liquid condition, and the degree of solubility of the oil and the solvent is affected by the temperature, the relative quantities of solvent and oil employed, the pressure, and the nature of the solvent.

This invention relates to an improved method of fractionating fatty oils by means of a relatively volatile, i. e. relatively low-boiling, solvent while the solvent is in the "paracritical state."

Relatively volatile solvents are employed for the reason that the solvents which are partially miscible with the oil while in the paracritical state ordinarily are those having critical temperatures no higher than 450° F., and it is desirable to avoid operating temperatures which might produce some thermal effect on the oil being treated.

In carrying out the improved fractionation process any fluid may be employed which is partially miscible, while in its paracritical state, with the oil to be treated, and does not react chemically with the oil. Such solvents include low-boiling hydrocarbons, such as methane, ethane, propane, the butanes, the pentanes, and the corresponding olefins, as well as mixtures thereof, such as a mixture of methane and normal butane, or a mixture of ethane and propane. Other agents include organic compounds such as halogenated hydrocarbons, including dichlor-

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difluor methane and methyl fluoride. Still other solvents which may be used are dimethyl ether, methyl ethyl ether, carbon dioxide, and ammonia.

The low-boiling normally gaseous paraffin hydrocarbons are preferred solvents because of their lower cost and relative inertness, and because they are miscible with most fatty oils to the desired degree. Propane is ordinarily preferred in carrying out the process but the other low-boiling hydrocarbons may be preferred in the treatment of certain oils. It may be advantageous to modify the propane, or other hydrocarbon solvent employed, by the incorporation of a small amount of a different solvent. Furthermore, the employment of relatively impure materials, such as commercial propane containing small quantities of other hydrocarbons, principally ethane, is within the scope of the invention.

In accordance with the improved process of this invention the fatty oil is refined by fractionation treatment which separates the oil into three or more separate fractions having distinctly different properties. This treatment is carried out in at least two separate contacting zones.

It is a principal object of the invention to provide a process for continuously fractionating a fatty oil into three or more fractions in at least two separate contacting zones by means of circulating solvent while evaporating and condensing a smaller quantity of solvent than in previous processes for effecting the same fractionation. It is a further object to provide a continuous process for fractionating a fatty oil into three or more fractions in two or more separate contacting zones without evaporation of the solvent except for the purpose of separating the solvent from product fractions. Other objects of the invention will be apparent from the following more detailed description of the invention.

The invention will be described in detail with reference to the accompanying drawings, in which

(1) Figure 1 is a diagrammatic representation in elevation of an arrangement of apparatus for carrying out one embodiment of the improved process, with certain modifications,

(2) Figure 2 is a diagrammatic representation in elevation of an arrangement of apparatus for carrying out an embodiment of the invention in which the oil is fractionated into four product fractions, and

(3) Figure 3 is a diagrammatic representation in elevation of an arrangement of apparatus for effecting fractionation of a fatty oil into four

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fractions by a flow arrangement different from that of Figure 2.

Fig. 1 illustrates an arrangement of apparatus for fractionating a fatty oil into three product fractions, in accordance with the improved process of this invention. This operation produces a relatively large intermediate fraction which is light in color and substantially neutral, a relatively small first raffinate fraction comprising a concentration of the color bodies of the fatty oil, and a final extract fraction which is a concentration of fatty acids and other highly soluble components of the fatty oil. The relatively large intermediate fraction is a substantially refined oil and requires little, if any, further treatment prior to use as a refined oil. The relatively small first raffinate fraction may be a waste product fraction but ordinarily this small fraction contains a concentration of components which it is desirable to recover. The relatively small final extract fraction also may be a waste product fraction but this fraction also may contain valuable components which it is desirable to recover. For example, in the refining of soybean oil by the process represented by Fig. 1, the first raffinate fraction contains a relatively high concentration of lecithin and other phosphatides, and the final extract fraction contains, in addition to the fatty acids, a relatively high concentration of tocopherols and sterols. Each of the relatively small fractions represents a concentration of valuable components and may be converted into highly desirable products by further treatment.

In the process of Fig. 1, the first raffinate fraction and the final extract fraction are each ordinarily limited to a quantity equivalent to less than 10 per cent (by weight) of the fatty oil being treated. Preferably the first raffinate fraction constitutes no more than 5 per cent of the fatty oil, while the final extract fraction is limited to 2 per cent or less of the fatty oil. For example, in the refining of soybean oil the first raffinate fraction preferably is limited to 2 per cent or less of the fatty oil, while the final extract fraction is about 1 or 2 per cent of the fatty oil.

In the process illustrated in Fig. 1, a fatty oil is treated in an extraction zone provided by fractionating tower 10 to separate the first raffinate fraction, which is withdrawn from the bottom of tower 10. Extract oil, whose most soluble components comprise the most soluble components of the fatty oil, is withdrawn from the top of tower 10 as a part of the extract phase and further treated in a separate fractionating zone in tower 11 to separate such extract oil into a final extract fraction and the relatively large intermediate fraction of the fatty oil.

Tower 11 is arranged and equipped to provide intimate contact of the extract oil and solvent under conditions which effect close fractionation of the oil, i. e. concentration in the extract of components undesired in the intermediate product, or desired to be concentrated in the final extract product. To this end, fractionating tower 11 is substantially elongated vertically and is provided with contact means, such as trays, baffles or packing, to effect intimate contact of counter-flowing liquid phases. Tower 11 also is provided with means for effecting extensive refluxing of the tower with extract oil. Such refluxing is effected by means of heating coils 12, which heat the extract phase as it flows up the tower to precipitate oil from the

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extract phase, or it may be provided by separating a portion of extract oil from the extract phase and returning it to the upper part of tower 11, i. e. external refluxing.

The initial extraction treatment of the fatty oil to separate a first raffinate, containing a concentration of the color bodies, may be carried out under any suitable conditions, but it is preferred to effect substantially complete removal of color bodies and a high concentration of other components of lesser solubility in the first raffinate product by subjecting the fatty oil initially to fractionation treatment under conditions substantially equivalent to those provided by tower 11. Consequently, tower 10 is generally similar to tower 11 in the provision of the various means for achieving close fractionation, i. e. substantial segregation of the less soluble components of the fatty oil in the raffinate, and vice versa.

In the normal operation of fractionating tower 10 a solvent stream consisting essentially of propane or other suitable solvent is introduced into the tower at a point near the bottom thereof, through line 15. The solvent stream is heated or cooled to the temperature desired in the bottom of the tower, by means indicated at 16, and line 15 is provided with a pump 17 to overcome the pressure maintained on tower 10. A stream of the fatty oil to be treated, such as soybean oil, is introduced into tower 10 at one or more intermediate points, as through line 18. The operating conditions imposed on tower 10 are such that, at equilibrium conditions, the fatty oil is only partly soluble in the upflowing solvent stream. As a result of the difference in gravity between the undissolved oil phase and the solvent phase, the undissolved oil phase flows downwardly in counter-current contact with the upflowing solvent phase. The solvent phase flows upwardly toward an overhead drawoff line at 19 while the oil, or lower, or raffinate, phase flows downwardly toward a bottoms drawoff line at 20. The upflowing solvent phase contains all but a small proportion of the solvent introduced from line 15 and a portion of the fatty oil. This phase also may be designated as the propane phase, or upper phase, or extract phase. The lower, or oil phase contains only a small proportion of the solvent and a portion of the oil in a solvent:oil ratio much lower than that existing in the solvent phase.

The volumetric ratio of solvent and oil introduced into tower 10 should be not lower than about 6:1 and preferably should be at least 10:1, for example, 15:1 to 30:1, or higher. Tower 10 is maintained under sufficient pressure to maintain the solvent substantially entirely in liquid condition. The operation essentially requires contact of the liquid solvent phase with the liquid oil phase, but the formation of a small quantity of solvent vapor is not objectionable so long as it does not interfere with the flow of the liquid phases in counter-current contact through and out of the tower. Since the operation of tower 10 essentially involves withdrawing the major portion of the fatty oil in the extract phase, the maximum temperature in the tower ordinarily is substantially lower than the critical temperature of the solvent. The critical temperature of propane is 206.3° F., whereas the critical pressure is 617.4 p. s. i. Consequently, when using propane as the solvent a maximum operating pressure of 400-700 p. s. i. is satisfactory.

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Tower 10 is divided into two zones by the introduction of the fatty oil from line 18 at an intermediate point. The upper zone, lying above this point, is the rectification zone in which the operation of the tower is directed substantially entirely to achieving the desired degree of fractionation of the constituents of the fatty oil which are absorbed in the solvent phase at lower points in the tower. The lower zone, lying below the oil charge point, is primarily a stripping zone in which the undissolved fatty oil and oil precipitated in the rectification zone are subjected to the stripping action of the upflowing stream of solvent, to dissolve in the solvent phase all constituents of the fatty oil except those which it is desired to include in the first raffinate fraction, to be withdrawn through line 20.

Rectification may be effected by heating the solvent phase, as it flows upwardly past the oil charge point to the top of the tower, to a temperature above the temperature in the bottom of the tower. Since the lowest temperature in the solvent phase is substantially higher than the temperature of maximum solubility of the oil and solvent, and since the solvent phase is saturated with oil at the lower temperature, the heating of the solvent phase to a higher temperature as it flows up the tower results in a decrease in density of the solvent and a corresponding precipitation of a part of the oil previously dissolved. This precipitated oil forms a new raffinate phase which flows down the tower in counter-current contact with the solvent phase, to effect further rectification of the oil.

Any suitable means may be employed for heating the solvent phase as it flows up the tower, but ordinarily this is effected by heating coils 14 which are located at suitable intervals in that portion of the tower in which it is desired to maintain a temperature gradient. The temperature differential between the top and bottom of tower 10 may vary from 1° F. to 60° F. The temperature gradient employed may be concentrated entirely between the oil charge point and the top of the tower or it may extend from top to bottom of the tower. Conveniently, a relatively small temperature gradient may be imposed on the stripping zone, while a larger temperature gradient is imposed on the rectification zone.

Alternative to the maintenance of a temperature gradient in tower 10, or in combination with that method, the tower may be refluxed by the return to the top of the tower of a portion of the extract oil. According to this method all, or a portion, of the extract phase withdrawn through line 19 is diverted through line 21 which connects with a separator 22. The pressure on the extract phase flowing through line 21 is substantially reduced by means of valve 23 to effect vaporization of the greater part of the solvent contained in the extract phase. To assist in this operation heating means 24 may be provided in line 21. In vessel 22 the liquids and vapors are separated and the solvent vapors pass overhead through line 25, which connects with solvent storage vessel 26. A cooler 27 is provided in line 25 to condense the solvent vapors.

The removal of solvent from the extract phase in vessel 22 may not be complete, and it is preferable not to remove the solvent completely since this requires excessive reduction in pressure at 23 or excessive heating, and since the return of a small part of the solvent in the reflux liquid

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does not interfere with the operation of tower 10. For example, if tower 10 is operated with a propane solvent at about 600 p. s. i., the pressure may be reduced at 23 to about 200 p. s. i., heat being supplied at 24 to replace heat of evaporation. This effects a sufficient removal of solvent and simplifies condensation of the solvent vapors at 27.

The reflux liquid, comprising extract oil and a small amount of the solvent, is collected in the bottom of vessel 22 and withdrawn therefrom through line 28 by means of pump 29. All, or a portion, of this oil is diverted from line 28 through line 30 for return to the top of tower 10.

The refluxing of tower 10 by the return of extract oil through line 30 is not essential to the operation of tower 10 as reflux oil from other sources may be introduced into the top of tower 10. For example, a suitable portion of raffinate phase produced in tower 11 may be collected and returned to the top of tower 10, by means not shown. Moreover it may be desirable to avoid all external refluxing, relying only on the refluxing provided by the temperature gradient to effect the desired rectification of the extract.

Conditions of temperature and pressure in tower 10 are regulated to distribute to the raffinate phase which collects in the bottom of tower 10, only a minor proportion of the fatty oil. In the two-zone system of operation illustrated by Fig. 1 it is desirable ordinarily to limit the proportion of the oil in the raffinate phase withdrawn through line 20 to the maximum proportion which is necessary to remove the color bodies and other relatively insoluble constituents from the extract. This will require ordinarily a raffinate containing not more than about 5 per cent of the fatty oil and, in the treatment of certain oils, such as soybean oil, this proportion may be 2 per cent or less. However, it may be desirable to operate tower 10 to produce a raffinate containing a substantially larger, although minor, proportion of the fatty oil. For example, it may be desirable to operate tower 10 to produce a raffinate oil representing a concentration of the more unsaturated glyceride components of the fatty oil for use as a drying oil. For this purpose it may be desirable to produce a raffinate oil in tower 10 representing 15 percent, or more, of the fatty oil charged to tower 10. Ordinarily, however, the production of such a drying oil fraction is effected in a three-zone arrangement, to be described below.

The exact operating conditions selected for tower 10 depend upon the character of the oil being treated and the proportions of oil and solvent employed, as well as the desired distribution of the oil between the raffinate and extract. The smaller the proportion of the fatty oil desired in the raffinate, the lower will be the temperature desired in the bottom of the tower. On the other hand, a relatively high ratio of solvent to oil charged to tower 10 requires a higher bottom temperature in the tower to counteract the greater solvent power in the relatively large proportion of solvent. The temperature in the top of tower 10 is sufficiently higher than the bottom temperature to provide the desired temperature gradient, and the introduction of reflux liquid from line 30 requires a somewhat lower top temperature than would be required in the absence of external refluxing. If no temperature gradient is imposed on tower 10, and the tower is refluxed externally to effect

rectification, the tower temperature necessarily must be substantially lower than in the absence of such external rectification, in order to incorporate the desired proportion of the fatty oil in the raffinate. In general, the bottom temperature controls the amount of oil rejected to the raffinate phase for withdrawal as bottoms, while the top temperature controls the amount of oil withdrawn overhead to produce the extract oil to be withdrawn and reflux oil to be returned to the tower. In the treatment of soybean oil to remove a small raffinate as a concentration of color bodies the temperature in the bottom of tower 10 will fall within the range of 140–190° F., while the temperature at the top of the tower will be in the range of 150–200° F.

The extract oil from tower 10 is further fractionated in tower 11 to separate it into a raffinate comprising a major portion of the oil charged to tower 11, and an extract containing a portion of the oil charged to tower 11. In accordance with a preferred modification of the process of Fig. 1 the portion of the extract phase withdrawn through line 19, and not diverted through line 21 for production of reflux liquid, is passed on through control valve 31 to an intermediate point of tower 11. Tower 11 is similar to tower 10 in construction and in the provision of means for effecting contact of counter-flowing liquid phases, heating the extract phase, and external refluxing. A solvent stream is drawn from reservoir 26 by means of line 32 and introduced into tower 11 at a low point. Line 32 is provided with pump 33 and temperature control means 34. Tower 11 is operated at somewhat higher temperatures than is tower 10, as it is desired to include in the final extract phase a substantially smaller proportion of the fatty oil than has previously been dissolved in tower 10. Tower 11 preferably is operated with a temperature gradient, and under these conditions the bottom temperature will be in the range 160–195° F., while the top temperature is in the range 165–210° F., although in certain cases an even higher top temperature may be imposed on tower 11.

Heating means 35 are provided in line 19 to regulate the temperature of the solvent phase from tower 10 introduced into tower 11 through line 19. The temperature of this liquid may be brought to the temperature desired to be maintained in tower 11 at the point of introduction, or the liquid from line 19 may be heated to an even higher temperature to assist in heating the solvent phase flowing upwardly in tower 11 toward the outlet of line 19.

Tower 11 conveniently is maintained under a sufficiently lower pressure than tower 10 in order to permit flowing the solvent phase from tower 10 directly through line 19 into tower 11. Preferably tower 11 is maintained substantially at the pressure required to prevent substantial vaporization of the solvent in the tower. This requires maintaining tower 10 under a pressure substantially higher than the minimum required to maintain liquid conditions, since tower 10 is at a lower temperature than tower 11. However, this does not adversely affect the operation of tower 10, since the maximum temperature of tower 10 does not extend ordinarily to a level at which the density of the solvent is greatly affected by variations of pressure.

However, in tower 11 it is desired to maintain the pressure as low as possible. In the operation of tower 11 it is advantageous to provide rectifi-

cation by imposing a temperature gradient on the tower, while limiting external refluxing to the minimum. Furthermore, the percentage of the oil in the tower which is permitted to remain in the final extract solution is relatively small, whereby it may be necessary to impose a relatively high temperature at the top of the tower. Consequently, the temperatures in tower 11 may extend into the region in which the density of the solvent is greatly affected by variations in pressure, and in which the change in density of the solvent produced by a change in the temperature is at a maximum at the lowest pressure necessary to prevent substantial vaporization of the solvent.

Operating conditions in tower 11 are adjusted to form a secondary raffinate phase, in the bottom of the tower, which contains oil equivalent to a major proportion of the oil charged to the tower through line 19. For example, in the treatment of soybean oil by the two-zone system of operation of Fig. 1, the oil charged to tower 11 may be distributed to the secondary raffinate in the bottom of the tower in an amount equivalent to approximately 90 per cent of the oil charged to tower 11 and equivalent to a major proportion of the oil charged to the system through line 18. For example, when tower 11 is operated to produce a first raffinate product, to be withdrawn through line 20, equivalent to less than 10 per cent of the fatty oil introduced through line 18, the second raffinate product accumulated in the bottom of tower 11 may contain oil equivalent to at least 80 per cent of the fatty oil from line 18. Ordinarily in the refining of soybean oil this two-zone process will involve distributing not more than 5 per cent of the fatty oil to the first raffinate product and at least 93 per cent to the second raffinate product. In accordance with one specific embodiment of the invention as applied to treatment of soybean oil, the first raffinate product withdrawn through line 20 may be limited to 2 per cent or less, while the second raffinate product, collected in the bottom of tower 11, may comprise 96 per cent or more of the fatty oil introduced into the system through line 18.

The solvent introduced into the bottom of tower 11 from line 32 functions principally in that tower to strip from the lower phase flowing down the tower such components of the oil as are undesired in the second raffinate product, and include these undesired components in the final extract product, along with other relatively soluble components of the oil which may be desired in the final extract product. Ordinarily solvent should be introduced into tower 11 from line 32 in a volumetric ratio of solvent from line 32 to oil introduced from line 19 of at least 6:1, and preferably at least 10:1.

The final extract phase flows out of the top of tower 11 through line 36 to a separating vessel 37. The pressure is reduced substantially at valve 38 in line 36 to permit evaporation of at least the greater part of the solvent. To assist this operation heat is applied at 39. Solvent vaporized in this way is separated from the remaining liquid in vessel 37 and is withdrawn overhead for recirculation in the system through line 40, which connects with line 25. The liquid collected in the bottom of vessel 37 is withdrawn through line 41 for recovery and further treatment of the oil product fraction contained therein. If necessary, a portion of this liquid may be returned as reflux liquid to the top of tower 11

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through line 42, which is provided with a pump 43.

The second raffinate product fraction is withdrawn from the bottom of tower 11 through line 44, which connects with a separating vessel 45. Pressure on this material is released by valve 46 sufficiently to effect evaporation of at least the greater part of the solvent, heat being applied at 47 to assist evaporation. Solvent separated in vessel 45 is withdrawn overhead and recirculated in the system through line 48, which connects with line 40. The liquid separated in the bottom of vessel 45 is withdrawn through line 49 for further treatment and recovery of the oil product fraction contained therein.

According to the preferred modification of the process of Fig. 1, as described above, the extract phase from the top of tower 10 is passed to tower 11 through line 19 without the separation of any of the solvent contained therein except for the production of reflux liquid in tower 10. Preferably it is desired to avoid evaporation of solvent from the extract phase of tower 10 even to this extent, since it is possible to provide refluxing of tower 10 by means of a temperature gradient in the tower or by means of reflux liquid obtained from some other external source, as mentioned above. It is advantageous to introduce into tower 11 as much as possible of the solvent contained in the extract phase from tower 10. One advantage is that fractionation of the oil in tower 11 appears to be assisted by the presence of the propane accompanying the oil charged from line 19. Another advantage will be described in more detail below.

Nevertheless, the process includes, as one modification, the substantial separation of solvent at 22 from all or a substantial portion of the extract oil transferred from tower 10 to tower 11. For this purpose line 28 connects with line 19, as shown, whereby oil containing a relatively small amount of solvent in admixture therewith may be transferred from vessel 22 to tower 11 for further fractionating treatment.

In accordance with a further modification of the process of Fig. 1, the extract phase liquid flowing through line 19 may be treated to effect a preliminary separation thereof into separate liquid phases which are separately introduced into tower 11 at different points. In this modification extract solution flowing through line 19 is diverted therefrom through line 50, which connects with vessel 51. Heating means 52 are interposed in line 50 to heat the extract solution flowing through line 50 to a substantially higher temperature to precipitate a separate liquid phase. The resulting mixture is permitted to settle in vessel 51 to form two separate phases. The upper phase, which now contains a smaller amount of oil, is withdrawn through line 53 and introduced into tower 11 at a point which may be somewhat below the connection of line 19 with tower 11. The lower phase liquid in vessel 51 contains much less solvent than was present in the extract solution in line 19. This liquid is withdrawn through line 54, which connects with line 19, whereby this liquid is introduced into tower 11 at a point which may be substantially above the point of introduction of the upper phase material from vessel 51. Cooling means 55 and 56 are provided in lines 54 and 53 to adjust the temperatures of these liquids to those at which they are desired to be introduced into tower 11. In this modification all, or substantially all, of the extract solution from line 19 is

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thus diverted through line 50 by suitable manipulation of valve 57 in line 50 and valve 58 in line 19. The phases separated in vessel 51 are thus introduced into tower 11 when the extract phase is heated, at 52, to a temperature sufficiently high to precipitate all but a small proportion of the oil. Alternatively, a smaller proportion of the oil may be precipitated and the lower phase liquid from the bottom of vessel 51 may then be introduced into tower 11 at a lower point than the point of introduction of the upper phase material from vessel 51.

In accordance with the improved process of this invention the stream of solvent for use in tower 10 is provided by continuously diverting a portion of the final extract phase flowing from the top of tower 11 through line 36. For this purpose line 15 is provided to connect line 36 with the lower part of tower 10. Since the temperature desired in the bottom of tower 10 ordinarily is substantially lower than the temperature at which the final extract phase emerges from tower 11, cooling means are provided at 16 in line 50 to cool the final extract phase flowing therethrough to the temperature desired in the bottom of tower 10. Preferably pump 17 is placed downstream from cooler 16 in order that the pump may act upon the cooled stream. In connection with this invention it has been found that the final extract phase produced by tower 11 and containing, as a result of the close fractionation therein, a concentration of only the most soluble components of the fatty oil being treated is substantially as effective a solvent treating agent in tower 10 as a stream of an equivalent volume of pure solvent. The oil components contained in the final extract phase liquid flowing through line 15 are present in such small concentration and are so highly soluble, particularly after the cooling step at 16, that they have no appreciable effect on the action of the solvent portion of this liquid in treating the fresh fatty oil charged from line 18 in tower 10.

This method of operation has the advantage that it permits limiting the vaporization of the solvent to the minimum quantity necessary for recirculation in relatively pure form to the bottom of tower 11 through line 32, or to the quantity necessary to be recovered from liquid products withdrawn through lines 20, 28, 41 and 49.

In this method of operation two essentially separate solvent treatments are effected by means of a single circulating stream of propane, represented by the propane introduced into reservoir 26 from line 25 and passed from reservoir 26 to tower 11 through line 32. This is an important advantage, since recovering the solvent by evaporation and condensation represents a substantial proportion of the operating cost of the refining process.

This method of operation has the further advantage that it permits employing in tower 10 substantially any desired solvent:oil ratio. Substantially all the solvent introduced into tower 10 from line 15 flows back again to tower 11 through line 19. If valve 38 in line 36 is controlled to provide for removal of a desired quantity of final extract phase for recovery of the final extract product fraction the quantity of final extract solution returned through line 15 for reuse in tower 10 may be varied at will, by control pump 17, without unduly disturbing the operation of the system.

According to an illustrative embodiment of the process of Fig. 1, 100 volumes of fatty oil

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introduced into tower 10 from line 13 in a unit of time are treated with 1800 volumes of liquefied propane introduced into tower 10 from line 13. Tower 10 is operated to distribute 2 parts, by weight, of the oil to the first raffinate product fraction withdrawn through line 20. The remainder of the fatty oil and substantially all of the propane pass overhead through line 19 and are transferred directly to tower 11 for further treatment. Into tower 11 1000 volumes of propane, from reservoir 26, are introduced through line 32 to complete the stripping operation in that tower, as described above. Approximately 100 volumes of propane are withdrawn from tower 11 in the secondary raffinate phase through line 44. The remaining 2700 volumes of propane pass overhead in the final extract phase through line 36. One-third of this final extract phase passes to vessel 37 for recovery of solvent and the final extract product fraction of the oil. Two-thirds of the final extract fraction, containing 1800 volumes of propane, are returned to tower 10 from line 36 by being diverted through line 15. The operation of tower 11 is controlled to include in the final extract fraction a proportion of the oil such that the amount recovered at 37 for withdrawal from the process through line 41 is equivalent to 1 part by weight of the 100 parts of oil charged to the process through line 13. Consequently, the 1800 volumes of propane returned to tower 10 through line 15 contain only 2 parts of oil, and this oil is combined with the oil extracted in tower 10 whereby the extract phase passing out of tower 10 through line 19 contains 100 parts of oil and approximately 1800 volumes of propane. In this example tower 10 is operated at a propane:oil ratio of approximately 18:1 whereas tower 11 is maintained at a propane:oil ratio of approximately 10:1. The 1000 volumes of propane charged into the bottom of tower 11 are recovered by vaporization at 37 and 45. The volumes of propane indicated in this example merely illustrate an approximate distribution of propane in the system and do not take into account the relatively small quantities of propane which are recovered in secondary recovery operations on the product fractions and small quantities of make-up propane which are introduced into reservoir 26 from line 59 to replace inevitable losses.

Since the oil contained in the solution flowing through line 15 represents a highly soluble small proportion of the fatty oil, and since the solubility of this small proportion of oil is greatly increased by the cooling step at 16, the proportion of oil in the solvent stream introduced into the bottom of tower 10 from line 15 may be substantially increased over that indicated in the foregoing illustrative embodiment. However, best operation of the process involves controlling the operation of tower 11 to restrict the amount of oil included in the final extract phase. For this reason it is desirable to operate tower 11 substantially without the return of external reflux oil through line 42, or with the smallest amount of external refluxing necessary to produce suitable rectification of the product oil fraction. Any product oil desired for rectification through line 42 must be carried overhead in solution through line 36. Increasing the quantity of oil in line 36 to provide reflux oil at 37 also involves a corresponding increase in the concentration of oil in the solution diverted from line 36 through line 15. For example, if in the

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foregoing illustrative embodiment it were desired to return a quantity of reflux oil to tower 11 through line 42 equivalent to the quantity of product oil withdrawn from the process through line 41, this would result in doubling the concentration of oil in the solution flowing through line 15.

In a further modification of the process of Fig. 1, the solvent stream flowing through line 15 to the bottom of tower 10 may be supplemented by a small quantity of relatively pure solvent diverted from line 32 through line 50. In this operation it may be desirable to introduce the solution from line 15 into tower 10 at a somewhat higher point, as through line 61.

For a specific example of the application of the improved process reference may be made to a refining treatment of a crude soybean oil having a fatty acid content of 0.23 per cent. This oil was charged continuously to an extraction and decolorizing tower similar in construction and operation to tower 10 of Fig. 1 and subjected in that tower to operating conditions designed to produce a first raffinate fraction containing 2.5 weight per cent of the charge oil. This tower was held under a pressure of 585 p. s. i., and temperatures of 168° F., 164° F., and 163° F. were maintained at the top, oil charge point, and bottom, respectively. The final extract phase produced in this tower was passed continuously to a second fractionating tower similar in construction and operation to tower 11 of Fig. 1. In this second tower the extract phase was subjected to treatment at substantially higher temperatures, and the tower was refluxed with a temperature gradient and by the return of external reflux oil. Fresh liquefied propane was introduced into the bottom of this second tower in a manner similar to the introduction of fresh propane into the bottom of tower 11 of Fig. 1 from line 32. The second fractionating tower was regulated as to operating conditions to produce a second raffinate product in the bottom of the tower containing 95.5 weight per cent of the oil charged to the first fractionating tower. The second tower was held under a pressure of 590 p. s. i., and temperatures of 195° F., 181° F., and 169° F. were maintained at the top, oil charge point, and bottom, respectively. The fresh propane was charged to the bottom of the second tower at a rate of 3280 volumes per 100 volumes of oil charged to the first tower. The extract solution from the top of the first tower contained 2780 volumes of propane per 100 volumes of oil charged to the first tower. Approximately 100 volumes of propane per 100 volumes of charge oil were included in the second extract phase withdrawn from the bottom of the second tower. The final extract solution withdrawn from the top of the second tower contained 5960 volumes of propane per 100 volumes of oil charged to the first tower. A portion of the final extract solution containing 3180 volumes of propane was diverted and treated to vaporize the propane and separate liquid oil for withdrawal as the final extract product and for return as reflux liquid to the top of the second tower. The remaining portion of the final extract phase from the top of the second tower, containing 2780 volumes of propane per 100 volumes of fresh charge oil, provided the solvent stream introduced into the bottom of the first tower. The second fractionating tower was refluxed externally by the return of approximately 11 parts of oil per 100 parts of fatty oil charged

to the first tower, and the extract oil from the top of the second tower was withdrawn as product at the rate of 2 parts by weight per 100 parts of oil charged to the first tower. This required operating the second tower to include in the final extract phase approximately 25 parts by weight of oil per 100 parts of fatty oil charged to the first tower. Consequently, the solvent stream introduced into the bottom of the first tower contained approximately 12 parts of the final extract oil per 100 parts of oil charged to the first tower. This operation produced a substantially refined soybean oil equivalent to 95.5 weight per cent of the crude oil, of light color and containing only 0.09 per cent fatty acids. The final extract product oil withdrawn from the top of the second tower contained 5.0 weight per cent fatty acids and was a concentration of sterols, tocopherols, and other similar constituents of the soybean oil. The first raffinate product withdrawn from the bottom of the first tower was a concentration of the color bodies of the crude soybean oil and also contained phosphatides, such as lecithin, in high concentration. This operation thus produced, through the operation of essentially a single circulating stream of solvent, a separation of the crude soybean oil into three fractions representing a lecithin concentrate, a sterol and tocopherol concentrate, and a substantially refined oil of good color.

The improved process also is applicable to the separation of a fatty oil into four fractions, as by the use of three fractionating towers. One embodiment of this modification is illustrated in Fig. 2 in which fractionating tower 10a is arranged to function substantially in the same manner as tower 10 of Fig. 1. In this modification the first fractionating tower 10a preferably is operated to separate as the first raffinate in the bottom of the tower a relatively small fraction, i. e. not more than about 10 per cent, and preferably 5 per cent or less, of the oil charged to the process through line 18a. This small fraction represents a concentration of the color bodies and other relatively insoluble components of the oil, and is withdrawn from the process through line 20a. The modification of Fig. 2 differs from that of Fig. 1 in that the extract oil withdrawn overhead from tower 10a through line 19a is subjected to a preliminary fractionation to produce an intermediate raffinate product, prior to being passed to tower 11a for the production of the small final extract fraction.

This intermediate fractionation of the extract oil from tower 10a is provided in tower 62, which is similar in construction and operation to towers 10a and 11a, being provided with means for promoting intimate contact of counter-flowing liquid phases and being provided with heating coils 63 for control of temperature and the maintenance of a temperature gradient. In Fig. 2 apparatus for supplying external reflux oil to towers 10a, 62 and 11a has not been shown, for simplicity of presentation. It will be understood, however, that any or all fractionating towers of Fig. 2 may be subjected to external refluxing in the manner described in connection with towers 10 and 11 of Fig. 1.

In Fig. 2 the parts whose function and operation are generally similar to corresponding parts of Fig. 1 are indicated by similar reference numerals, with the subscript "a." The description of such parts in Fig. 1 applies also to the

corresponding parts of Fig. 2, except as modified in the description of Fig. 2.

In accordance with the modification of Fig. 2 the extract solution withdrawn from the top of tower 10a through line 19a is passed to an intermediate point of tower 62. Alternatively, all or a portion of the solution flowing through line 19a may be diverted through line 50a, and heated to a substantially higher temperature by heating means 52a to effect the formation of separate liquid phases. The phases are separated in vessel 51a and separate phases are withdrawn through lines 53a and 54a for separate introduction into tower 62 in the manner described in connection with the separate phases withdrawn from vessel 51 of Fig. 1.

Tower 62 is operated to separate the oil introduced therein into a relatively small intermediate raffinate fraction representing a concentration of the more unsaturated components of the oil. For example, in the refining of soybean oil by the modification of Fig. 2, tower 62 may be operated to separate an intermediate raffinate fraction representing 15 to 35 per cent of the oil charged to the process through line 18a. The intermediate raffinate fraction thus produced has an increased value as a drying oil and is of good color by reason of the removal of color bodies from the oil in tower 10a. Such a drying oil fraction separated from a crude soybean oil in the method of Fig. 2 has an iodine number of 145 to 155, while the remaining oil carried overhead in solution in tower 62 has a substantially lower iodine number of 125 to 135.

Tower 62 is operated at temperatures intermediate to those imposed on tower 10a and tower 11a, and the tower may be subjected to external refluxing if desired. The intermediate raffinate product is withdrawn from the bottom of tower 62 through line 54, which discharges into a separator 65. Pressure is released at valve 66 sufficiently to evaporate the solvent which separates from the remaining liquid in vessel 65. The solvent vapors pass overhead through line 67, which connects with solvent reservoir 26a. A cooler 27a is provided to condense the solvent vapors prior to introduction of the solvent into vessel 26a. The intermediate extract fraction is withdrawn from the bottom of vessel 65 through line 68 for further treatment for the recovery of the oil contained therein.

The extract solution is withdrawn from the top of tower 62 through line 69, which connects with a tower 11a at an intermediate point. Tower 11a is operated substantially exactly in the manner described in connection with tower 11 of Fig. 1, to separate the oil introduced into tower 11a into a relatively large final raffinate product and a relatively small final extract product. The operating conditions for tower 11a ordinarily differ somewhat from those applied in tower 11 in the two-zone process of Fig. 1, since the final extract fraction to be removed overhead in tower 11a ordinarily represents a larger proportion of the oil charged to tower 11a than the proportion of oil charged to tower 11 represented by the final extract product produced by that tower. Thus control of tower 11a ordinarily is easier than control of tower 11, since the ratio of the extract product to the raffinate product is somewhat larger than in tower 11.

The raffinate phase separated in the bottom of tower 11a is withdrawn through line 44a which connects with a separating vessel 45a. Pressure

is released by valve 46a whereby the solvent contained in this raffinate product is largely evaporated and separated overhead as a vapor in vessel 45a. The solvent vapors are returned for reuse through line 48a, which connects with line 67. The final raffinate product, produced in tower 11a, is withdrawn from vessel 45a through line 49a for further treatment, such as the removal of residual quantities of solvent, and other desired further refining steps. This product is, however, except for the presence of solvent, a substantially refined oil of good color in which the fatty acid content has been reduced to the amount which is readily removable by moderate steam stripping.

The final extract phase is withdrawn from the top of tower 11a through line 36a, which connects with separating vessel 37a, and is provided with a valve 38a and heating means 39a. This equipment is operated in the same manner as similar equipment shown in Fig. 1 whereby the solvent is largely evaporated and withdrawn from vessel 37a through line 40a which, in this arrangement, is connected with line 67 for recirculation of the solvent. The final extract product is withdrawn through line 41a for further treatment, such as the removal of residual quantities of solvent, and other desired refining steps. This fraction represents a high concentration of the fatty acid content of the fatty oil being treated, and also a high concentration of the sterol and tocopherol content of the fatty oil.

A portion of the final extract phase flowing through line 36a is diverted through line 15a, which is provided with cooling means 16a and a pump 17a. Line 15a connects with tower 10a at a low point in order to supply to tower 10a a stream of solvent, in a manner analogous to the operation of line 15 and tower 10 in Fig. 1. A sufficient quantity of final extract phase is diverted through line 15a to provide a solvent stream for tower 62 also. The solvent stream for tower 62 is diverted from line 15a through line 69, which is provided with cooling means 70 and a pump 71. Line 69 connects with tower 62 at a low point in order to supply the solvent stream to that tower in the manner described in connection with line 15 and tower 10 of Fig. 1. Line 69, cooling means 70, and pump 71 operate in a manner analogous to line 15, cooling means 16, and pump 17 of Fig. 1.

According to an illustrative embodiment the process of Fig. 2, 100 volumes of fatty oil introduced into tower 10a from line 18a in a unit of time are treated with 1800 volumes of liquefied propane introduced into tower 10a from line 15a. Tower 10a is operated to distribute 2 parts of the fatty oil to the first raffinate product withdrawn through line 20a. The remainder of the fatty oil and substantially all the propane pass overhead through line 19a and are transferred directly to tower 62 for further treatment. Into tower 62 1800 volumes of propane are introduced through line 69. Tower 62 is operated to separate an intermediate raffinate fraction equivalent to 30 parts of the oil charged to the process. This oil and about 30 volumes of propane are withdrawn from the process through line 64. The remainder of the oil introduced into tower 62, together with all the remainder of the propane, passes overhead and is introduced into tower 11a for treatment in the manner described. In tower 11a conditions are controlled to separate a final raffinate product comprising 66 parts of the oil charged to the process. This oil and approximately 70 volumes of propane are withdrawn from the process through

line 44a. Of the 3600 volumes of propane charged to tower 62 per 100 parts of oil charged to the process through line 18a, approximately 30 volumes are withdrawn from the bottom and the remaining 3570 volumes are introduced into tower 11a through line 69'. Into the bottom of tower 11a approximately 1000 volumes of propane are introduced through line 32a, which connects the bottom of tower 11a with reservoir 26a. Of the total of 4570 volumes of propane thus charged to tower 11a approximately 70 volumes are withdrawn from the bottom with the raffinate. The remaining 4500 volumes pass overhead in the final extract phase through line 36a. A portion of this final extract phase containing 900 volumes of propane passes to vessel 37a for recovery of solvent and the final extract product. The remaining 3600 volumes of propane are diverted through line 15a, and of this quantity 1800 volumes pass through line 69 to the bottom of tower 62, while 1800 volumes are introduced into the bottom of tower 10a. Since the propane passed to vessel 37a contains approximately 2 parts of the oil as the final extract product the 3600 volumes of propane diverted through line 15a are accompanied by approximately 8 parts of fatty oil per 100 parts of oil charged to tower 10a. This fatty oil is equally distributed between streams of solvent passing to towers 10a and 62. Consequently in the above operation the overhead extract phase withdrawn from tower 10a through line 19a contains approximately 1800 volumes of propane and approximately 102 parts of the fatty oil per 100 parts of oil charge. After the separation treatment in tower 62 the extract phase passing overhead from that tower through line 69' contains approximately 3570 volumes of propane and 58 parts of oil per 100 parts of the fatty oil charged to the process.

In a further modification of the process of Fig. 2, the solvent stream flowing through line 69 to the bottom of tower 62 may be supplemented by a small quantity of relatively pure solvent diverted from line 32a through line 72. In this operation it may be desirable to introduce the solution from line 69 into tower 62 at a somewhat higher point.

In a further modification of the process of Fig. 2, the solvent stream flowing through line 15a to the bottom of tower 10a may be treated to remove free fatty acids. In this operation all or a portion of the liquids flowing through line 15a are diverted through line 73. Alkali is introduced through line 74 and the resulting mixture passes through mixer 75 to a settler 76. In settler 76 the soaps formed are permitted to settle and are drawn off through line 77, while the resulting neutral solution is returned to line 15a through line 78. This modification has the advantage that the accumulation of fatty acids in the system is reduced and any soaps which are not removed by settling at 76 are subjected to two precipitation treatments in towers 10a and 62 prior to the final separation of the raffinate fraction of the oil in tower 11a, which may be intended for use as an edible oil.

A further modification of the application of the process to the continuous separation of the fatty oil into four fractions by the use of three fractionating towers is illustrated in Fig. 3. In this modification the first fractionating tower 18b preferably is operated to separate as the first raffinate in the bottom of the tower a relatively large minor portion of the fatty oil. For example, in the treatment of soybean oil charged to tower

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10b through line 18b operating conditions are controlled to separate a raffinate comprising a minor portion of the fatty oil charged to the tower and representing a concentration of the unsaturated components of the fatty oil, as well as a concentration of color bodies and other relatively insoluble components of the oil. In this modification tower 10b is operated under conditions effective to produce a raffinate comprising oil equivalent to 15 to 45 per cent of the fatty oil charged to tower 10, preferably 25 to 35 per cent. Tower 10b is constructed and arranged to function substantially in the same manner as tower 10 of Fig. 1. Tower 11b is constructed and arranged to function substantially in the same manner as tower 11 of Fig. 1 and tower 11a of Fig. 2. The operation of tower 11b closely resembles that of tower 11a, since the extract oil treated in tower 11b represents a fraction of the fatty oil generally similar to the fraction treated in tower 11a of Fig. 2. The modification of Fig. 3 differs from that of Fig. 1 largely in that the relatively large minor fraction of the fatty oil separated as raffinate in tower 10b is further treated in tower 79 to extract most of this raffinate in an intermediate extract product oil of good color and good drying qualities, while concentrating the color bodies and other less soluble components in a relatively small raffinate product separated in the bottom of tower 79. Tower 79 is similar in construction and arrangement to the other fractionating towers, being arranged to effect close fractionation of the oil into the desired fractions. Tower 79, like the other towers described, is substantially elongated vertically and is provided with contact means to facilitate contact of the counter-flowing liquid phases. Tower 79 is provided with heating coils 80 for control of temperature and the maintenance of a temperature gradient, and may also be provided with means for effecting external refluxing of the tower. In Fig. 3 apparatus for supplying external reflux oil to towers 10b, 11b and 79 has been omitted, for simplicity of presentation. It is to be understood, however, that any or all of these towers may be subjected to external refluxing in the manner described in connection with towers 10 and 11 of Fig. 1.

In Fig. 3 the parts whose function and operation are generally similar to corresponding parts of Fig. 1 are indicated by similar reference numerals, with the subscript "b." It will be understood that the description of such parts given above in connection with Fig. 1 applies also to similarly numbered parts of Fig. 3, except as modified by the description of Fig. 3.

The relatively large raffinate, comprising a minor fraction of the fatty oil, which is collected in the bottom of tower 10b is withdrawn therefrom through line 20b, which connects with tower 79 at an intermediate point. A solvent stream is introduced into tower 79 from line 81, and this solvent stream flows upwardly in tower 79 in counter-current contact with the downflowing oil phase, in the manner described above in connection with the other towers. Since tower 79 is provided to extract a major portion of the oil charged to the tower the operating temperature of tower 79 ordinarily is somewhat lower than that of tower 10b. Ordinarily operating conditions in tower 79 are regulated to restrict the final raffinate in this tower to less than 10 per cent, and preferably less than 5 per cent, of the fatty oil charged to the process through line 18b. This minor fraction, representing a concentration of color bodies and other less soluble components of

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the fatty oil, is withdrawn from tower 79 through line 82.

The extract phase formed in tower 79 is withdrawn overhead through line 83, which connects with separating vessel 84. Pressure on this extract phase is reduced at valve 85 to effect substantial evaporation of the solvent, heat being supplied by heating means 86 to facilitate evaporation. The solvent vapors are separated in vessel 84 and withdrawn overhead through line 87 which connects with line 40b, whereby the solvent is conveyed back to solvent reservoir 26b cooling means 27b being provided in line 40b to condense the solvent vapors. The liquid separated in vessel 84 is withdrawn through line 88 for further treatment, such as the removal of residual quantities of solvent, and other desired refining steps. This fraction is a drying oil of good color.

The extract phase produced in tower 10b is withdrawn overhead through line 19b, which connects with tower 11b at an intermediate point thereof. In tower 11b the extract oil is subjected to further fractionation treatment with relatively pure solvent introduced into the bottom of tower 11b through line 32b from reservoir 26b. Tower 11b is operated to separate the extract oil introduced into the tower into a relatively large intermediate fraction as a raffinate product and a relatively small final extract fraction comprising a concentration of the most soluble components of the fatty oil. The operation of tower 11b is generally similar to that of tower 11 and tower 11a, and the details of operation described in connection with those towers apply also to the operation of tower 11b. The relatively large raffinate produced in tower 11b is withdrawn from the bottom thereof through line 44b, which connects with a separating vessel 45b. Pressure is reduced at valve 46b whereby there is substantial evaporation of solvent which passes overhead in vessel 45b through line 48b to line 40b. The liquid separated in vessel 45b is withdrawn through line 49b for further treatment to recover the substantially refined fraction of light color and low fatty acid content.

The final extract phase formed in tower 11b is withdrawn overhead through line 36b, which connects with separating vessel 37b. Pressure is released at valve 38b and heat is supplied at heating means 39b to effect substantial evaporation of the solvent which passes overhead in vessel 37b through line 40b. A relatively small final extract fraction is withdrawn from the process from vessel 37b through line 41b. This fraction represents a concentration of fatty acids of the fatty oil and also a concentration of the tocopherol and sterol content of the oil.

A portion of the solvent phase flowing through line 36b is diverted therefrom through line 15b for transfer to the bottom of tower 10b as the solvent stream therefor. Line 15b is provided with cooling means 16b and a pump 17b whereby it functions in substantially exactly the same manner as line 15 of Fig. 1 and line 15a of Fig. 2. Another portion of the solvent phase flowing through line 36b is diverted through line 81 in order to supply a portion of the final extract phase to the bottom of tower 79 as the solvent stream therefor. Line 81 is provided with cooling means 89 and a pump 90 to effect transfer of the extract phase into tower 79 and to cool the extract phase to the lower temperature desired in the bottom of tower 79.

According to an illustrative embodiment of the

process of Fig. 3, 100 volumes of fatty oil are charged into the system through line 18b in a unit of time, while 1100 volumes of liquefied propane are introduced into the bottom of tower 11b through line 32b. Extract solution from the top of tower 11b is transferred through line 15b to the bottom of tower 10b at the rate of 1500 volumes of propane per 100 volumes of charge oil. Tower 10b is operated to distribute 30 parts of the oil contained therein to a first raffinate which separates in the bottom of tower 10b. This raffinate fraction, containing about 30 volumes of propane, is transferred through line 20b to tower 79. Extract solution from the top of tower 11b is introduced, through lines 36b and 81b, into the bottom of tower 79 at the rate of 500 volumes of propane per 100 volumes of oil charged to the process through line 18b. Tower 79 is operated to separate a final raffinate fraction containing 2 parts of the fatty oil which is withdrawn from the bottom of tower 79 through line 82. Substantially all the propane introduced into tower 79 passes overhead through line 83, and these 530 volumes of propane are recovered at 84 for recirculation to reservoir 26b. The 1500 volumes of propane introduced into the bottom of tower 10b from line 15b pass entirely to the extract phase withdrawn overhead, except for approximately 30 volumes which are included in the raffinate solution withdrawn through line 20b. The 1470 volumes of propane contained in the extract phase flowing from the top of tower 10b through line 19b are all introduced into tower 11b. The sum of this volume plus the volume of propane introduced into the bottom of tower 11b from line 32b is 2570. Tower 11b is controlled to separate a raffinate fraction equivalent to approximately 66 parts of fatty oil per 100 parts of fatty oil charged to the process through line 18b. This raffinate solution withdrawn from the bottom of tower 11b through line 44b also contains approximately 70 volumes of propane. The remainder of the propane introduced into tower 11b, 2500 volumes, is included in the extract solution withdrawn from the top of tower 11b through line 36b. As has been described, approximately three-fifths of this extract phase is diverted to tower 10b through line 15b, and one-fifth is diverted to tower 79 through line 81. The remaining one-fifth of the extract phase withdrawn from tower 11b is passed to vessel 37b for separation of the solvent from the product oil. The operating conditions of tower 11b are controlled whereby approximately 2 parts by weight of the fatty oil, per 100 parts of fatty oil charged to the process through line 18b, are recovered from solvent at 37b. Consequently, the solvent stream passed to tower 10b through line 15b contains 6 parts of fatty oil, while the stream flowing through line 81 contains 2 parts of fatty oil. Consequently, the extract phase flowing through line 19b to tower 11b contains 76 parts by weight of fatty oil per 100 parts of oil charged to the process through line 18b.

In accordance with one modification of the method of Fig. 3, all or a portion of the solvent stream for tower 79 may be provided in an alternative manner. In this modification a portion of the extract phase flowing through line 19b from tower 10b to tower 11b is diverted through line 91, which connects with a phase separating vessel 92. The extract phase material flowing through line 91 is heated by heating means 93 to a temperature sufficiently high to effect precipitation of the maximum possible proportion of the oil content thereof as a separate liquid phase.

The precipitated material settles out as a lower liquid phase in vessel 92. This material is withdrawn from the bottom of vessel 92 through line 94 which discharges into line 19b whereby the lower phase material separated in vessel 92 is subjected to fractionating treatment in tower 11b in the manner described. Cooling means 95 may be provided in line 94 to adjust the temperature. The upper phase is withdrawn overhead from vessel 92 through line 96. Line 96 connects with line 81 to effect transfer of the overhead phase material from vessel 92 to the bottom of tower 79 as all or a portion of the solvent stream for that tower.

In accordance with a further modification of the process of Fig. 3, the solvent stream flowing to tower 79 through line 81 is treated to remove fatty acids therefrom. In this modification the solvent stream is diverted from line 81 through line 97. Alkali is introduced into line 97 from line 98 and the resulting mixture flows through line 97 and mixer 99 to a settler 100. In settler 100 the soaps are permitted to settle and are withdrawn through line 101. The neutralized solvent stream is then returned to line 81 through line 102. This modification has the advantage that the fatty acid content of the solvent, which might otherwise be included in the drying oil fraction, is removed prior to contact of the solvent with the oil treated in tower 79.

In any of the above-described methods of operating the process of Fig. 3, tower 11b may be operated primarily to strip the raffinate product of the tower and produce a solvent stream at the top. In this operation no extract solution from tower 11b passes to vessel 37b for separation of oil, and the light portion of the fatty oil is all incorporated in the extract product of tower 79, except for fatty acids removed at 100.

In the foregoing detailed description of the improved process reference has been made to the refining of vegetable oils such as soybean oil, in which the final extract fraction is a concentration of tocopherols, sterols, and fatty acids. The process of the invention is applicable also to the treatment of vitamin-containing fish oils to separate a small final extract which is a concentration of the vitamin content of the charge oil. In the treatment of a vitamin oil in the processing arrangement of Fig. 1, the oil may be treated in tower 10 to separate a small raffinate fraction which is a concentration of the color bodies, and the decolorized extract oil is then further treated in tower 11 to separate a small final extract fraction containing the vitamins in high concentration. The raffinate fraction separated in tower 11 is a refined oil of good color which still may have sufficient vitamin potency for certain uses as a vitamin oil.

The processing arrangement of Fig. 1 also may be used in subjecting a vitamin oil to a two-stage concentrating treatment. In this arrangement tower 10 is operated under conditions effective to separate a raffinate comprising the bulk of the oil. A relatively small extract fraction is then passed to tower 11 for further concentration treatment to produce the final small extract. In this processing arrangement it may be desirable to operate tower 10 to separate an extract fraction containing only a little more of the oil than is desired in the final fraction containing the vitamin concentrate. For example, tower 10 may be operated to separate a raffinate containing 96 per cent of the oil. The 4 per cent extract oil from tower 10 is then fractionated in tower 11

into approximately equal portions, the raffinate fraction from tower 11 constituting the vitamin concentrate. This method of operation is based on the fact that the concentration of the highly soluble stearin content of vitamin oils in the final extract fraction makes it difficult to produce concentrates of high potency in the final extract. In this operation, by careful regulation of the operation of tower 11, the vitamin content of the oil is largely concentrated in the raffinate withdrawn from the bottom of tower 11 through line 44. The oil fraction recovered overhead from tower 11 and withdrawn through line 41 may then be subjected to refrigeration to separate the stearin from any oil included in the extract fraction. The stearin separated in this manner may be washed by means of relatively cold solvent from reservoir 26, prior to passage of the solvent to tower 11 through line 32, in order to recover and return to the system any vitamin-containing oil included in the final extract fraction from tower 11.

Any of these methods of treatment of fish oils by means of the processing arrangement of Fig. 1 may be carried out also in the processing arrangement of Fig. 2, with certain additional steps provided for by Fig. 2. For example, a fish body oil may be treated in accordance with the arrangement of Fig. 2 to separate a small color fraction at 20a, an intermediate drying oil fraction at 64, an intermediate edible oil fraction at 44a, and a vitamin fraction at 41a. Alternatively, towers 62 and 11a of Fig. 2 may be employed in a two-stage concentration treatment of decolorized extract oil from tower 10a, as described above in connection with Fig. 1.

The operating conditions and the material distributions described above in connection with the various modifications of the process illustrated by the drawings necessarily refer to conditions existing after equilibrium has been reached in the operation of the process. It will be understood that any of the available operating expedients may be employed for reaching equilibrium conditions. For example, in starting up the system represented by Fig. 1, tower 11 may be operated temporarily at a higher-than-normal top temperature until the oil recovered at 37 is of desired quality. Thereafter the temperature may be lowered gradually to increase the quantity of the oil distributed to the extract phase. Furthermore, all of the oil separated at 37 may be returned to the top of tower 11 through line 42 until the quality of the oil separated at 37 is satisfactory. Similar starting-up procedures may be applied to the other systems of operation illustrated in the drawings.

I claim:

1. A method for refining a fatty oil which comprises introducing said oil into a solvent extraction zone wherein said oil is contacted with a solvent for said oil which solvent is relatively volatile having a critical temperature not substantially higher than 450° F., maintaining the temperature in said extraction zone above the temperature of maximum solubility of the oil in the solvent and under a pressure effective to maintain the solvent substantially entirely in the liquid condition in the extraction zone, regulating the conditions of temperature and pressure in said extraction zone to form an extract phase containing a major proportion of said fatty oil and a raffinate phase containing a minor proportion of said fatty oil including a concentration of the color bodies of said oil, separately with-

drawing said extract and raffinate phases from said extraction zone, continuously passing a stream of said solvent in liquid condition upwardly in an elongated solvent fractionation zone from a lower solvent inlet to an upper extract phase outlet, introducing into said fractionation zone extract oil comprising at least a portion of the oil separated from said fatty oil by said extraction zone including at least a portion of the most soluble components of said fatty oil, introducing said extract oil into said fractionation zone and into contact with said solvent stream at a point below said extract phase outlet and substantially higher than said solvent inlet to form separate counter-flowing extract and raffinate phases, maintaining the lowest temperature in said fractionation zone above the temperature of maximum solubility of said extract oil in said solvent and applying sufficient pressure to said fractionation zone to maintain the solvent therein substantially entirely in the liquid condition, regulating temperature and pressure and the solvent:oil ratio in said fractionation zone to form a raffinate phase in the bottom thereof comprising oil equivalent to at least a major portion of said extract oil charged to said fractionation zone and to form an extract phase containing a portion of the extract oil charged to the fractionation zone, separately withdrawing said extract and raffinate phases from said fractionation zone, treating a portion of said last-mentioned withdrawn extract phase to recover solvent and a product oil fraction therefrom, segregating another portion of said last-mentioned withdrawn extract phase and adjusting the temperature and pressure thereof to a condition of greater solubility of said solvent and said fatty oil, and introducing said segregated portion of extract phase into said extraction zone to supply thereto at least a major portion of the solvent required in the said extraction treatment in said zone.

2. The method of claim 1 in which a liquefied normally gaseous solvent is employed.

3. The method of claim 1 in which liquefied propane is employed as the solvent.

4. The method of claim 1 in which the raffinate withdrawn from said extraction zone is limited to less than 10 weight per cent of the fatty oil, all the extract oil from the extraction zone is treated in the fractionation zone to form a raffinate phase therein containing oil equivalent to more than 80 weight per cent of the fatty oil, and less than 10 weight per cent of the fatty oil is recovered as a product oil fraction from the final extract phase formed in the fractionation zone.

5. The method of claim 1 wherein extract oil from the extraction zone is passed to the fractionation zone without substantial separation of accompanying solvent.

6. A method for refining crude soybean oil which comprises introducing said oil into a solvent extraction zone wherein said oil is contacted with a solvent for said oil which solvent is relatively volatile having a critical temperature not substantially higher than 450° F., maintaining the temperature in said extraction zone above the temperature of maximum solubility of the oil in the solvent and under a pressure effective to maintain the solvent substantially entirely in the liquid condition in the extraction zone, regulating the conditions of temperature and pressure in said extraction zone to form a raffinate phase containing not more than about 5 weight

per cent of the crude soybean oil charged to the extraction zone and an extract phase containing the remainder of the crude soybean oil, separately withdrawing said extract and raffinate phases from said extraction zone, continuously passing a stream of said solvent in liquid condition upwardly in an elongated solvent fractionation zone from a lower solvent inlet to an upper extract phase outlet, introducing the extract oil from the extraction zone into said fractionation zone and into contact with said solvent stream at a point below said extract phase outlet and substantially higher than said solvent inlet, maintaining the lowest temperature in said fractionation zone above the temperature of maximum solubility of said extract oil in said solvent and applying sufficient pressure to said fractionation zone to maintain the solvent therein substantially entirely in the liquid condition and form separate counter-flowing extract and raffinate phases, regulating temperature and pressure and the solvent:oil ratio in said fractionation zone to form a raffinate phase in the bottom thereof comprising oil equivalent to not less than about 93 weight per cent of the crude soybean oil charged to the extraction zone and to form an extract phase containing a portion of the extract oil charged to the fractionation zone, separately withdrawing said extract and raffinate phases from said fractionation zone, treating a portion of said last-mentioned withdrawn extract phase to recover solvent and a product oil fraction therefrom, segregating another portion of said last-mentioned withdrawn extract phase and adjusting the temperature and pressure thereof to a condition of greater solubility of said solvent and said fatty oil, and introducing said segregated portion of extract phase into said extraction zone to supply thereto at least a major portion of the solvent required in the said extraction treatment in said zone.

7. A method for refining a fatty oil which comprises introducing said oil into a solvent extraction zone wherein said oil is contacted with a solvent for said oil which solvent is relatively volatile having a critical temperature not substantially higher than 450° F., maintaining the temperature in said extraction zone above the temperature of maximum solubility of the oil in the solvent and under a pressure effective to maintain the solvent substantially entirely in the liquid condition in the extraction zone, regulating the conditions of temperature and pressure in said extraction zone to form an extract phase containing a major proportion of said fatty oil and a raffinate phase containing a minor proportion of said fatty oil including a concentration of color bodies of said oil, separately withdrawing said extract and raffinate phases from said extraction zone, continuously contacting extract oil from said extraction zone with another portion of said solvent in a second extraction zone at a temperature above the temperature of maximum solubility of the oil and the solvent to separate a second raffinate phase equivalent to a minor proportion of the fatty oil charged to the first-mentioned extraction zone, separately withdrawing extract and raffinate phases from said second extraction zone, continuously passing a stream of said solvent in liquid condition upwardly in an elongated solvent fractionation zone from a lower solvent inlet to an upper extract phase outlet, introducing the extract oil from said second extraction zone into said fractionation zone and into contact with said solvent

stream at a point below said extract phase outlet and substantially higher than said solvent inlet, maintaining the lowest temperature in said fractionation zone above the temperature of maximum solubility of said extract oil in said solvent and applying pressure to said fractionation zone to maintain the solvent therein substantially entirely in the liquid condition and form separate counter-flowing extract and raffinate phases, regulating temperature and pressure and the solvent:oil ratio in said fractionation zone to form a raffinate phase in the bottom thereof comprising oil equivalent to a major proportion of said fatty oil charged to said first-mentioned extraction zone and to form an extract phase containing a portion of the extract oil charged to the fractionation zone, separately withdrawing said extract and raffinate phases from said fractionation zone, treating a portion of said last-mentioned withdrawn extract phase to recover solvent and a product oil fraction therefrom, segregating two other portions of said last-mentioned withdrawn extract phase and adjusting the temperature and pressure thereof to conditions of greater solubility of said solvent and said fatty oil, and introducing said segregated portions of extract phase into said first-mentioned and said second extraction zones to supply to each zone at least a major portion of the solvent required in the said extraction treatment in each zone.

8. A method for refining a fatty oil which comprises introducing said oil into a solvent extraction zone wherein said oil is contacted with a solvent for said oil which solvent is relatively volatile having a critical temperature not substantially higher than 450° F., maintaining the temperature in said extraction zone above the temperature of maximum solubility of the oil in the solvent and under a pressure effective to maintain the solvent substantially entirely in the liquid condition in the extraction zone, regulating the conditions of temperature and pressure in said extraction zone to form an extract phase containing a major proportion of said fatty oil and a raffinate phase containing a minor proportion of said fatty oil, separately withdrawing said extract and raffinate phases from said extraction zone, continuously contacting raffinate oil from said extraction zone with another portion of said solvent in a second extraction zone at a temperature above the temperature of maximum solubility of the oil and the solvent to separate a final raffinate product containing a minor proportion of the oil introduced into said second extraction zone and an intermediate extract phase containing a major proportion of the oil introduced into said second extraction zone, separately withdrawing said extract and raffinate phases from said second extraction zone, continuously passing a stream of said solvent in liquid condition upwardly in an elongated solvent fractionation zone from a lower solvent inlet to an upper extract phase outlet, introducing the extract oil from said first-mentioned extraction zone into said fractionation zone and into contact with said solvent stream at a point below said extract phase outlet and substantially higher than said solvent inlet, maintaining the lowest temperature in said fractionation zone above the temperature of maximum solubility of said extract oil in said solvent and applying sufficient pressure to said fractionation zone to maintain the solvent therein substantially entirely in the liquid condition and to form separate counter-

flowing extract and raffinate phases, regulating temperature and pressure and the solvent:oil ratio in said fractionation zone to form a raffinate phase in the bottom thereof comprising oil equivalent to a major portion of said fatty oil charged to said first-mentioned extraction zone and to form an extract phase containing a portion of the extract oil charged to the fractionation zone, separately withdrawing said extract and raffinate phases from said fractionation zone, treating a portion of said last-mentioned withdrawn extract phase to recover solvent and a product oil fraction therefrom, segregating two other portions of said last-mentioned withdrawn extract phase and adjusting the temperature and pressure thereof to conditions of greater solubility of said solvent and said fatty oil, introducing said segregated portions of extract phase into said first-mentioned and said second extraction zones to supply to each zone at least a major portion of the solvent required in said extraction treatment in each zone.

9. In the refining of a fatty oil by a series of at least two paracritical fractionations with a low-boiling solvent having a critical temperature not substantially higher than 450° F., the improvement which includes the steps of: subjecting said fatty oil to a first fractionation into primary extract and raffinate phases in a first fractionation zone with a solvent comprised principally of said low-boiling solvent under temperatures in the paracritical range and under liquefying pressure; separately withdrawing said primary extract and raffinate phases and subjecting at least part of said primary extract to a subsequent fractionation into secondary extract and raffinate phases in a separate fractionation zone with additional solvent, said solvent being comprised principally of said low-boiling solvent, and said subsequent fractionation being carried out at paracritical temperatures higher than those prevailing in the first fractionation zone; separately withdrawing said secondary extract and raffinate phases from said separate fractionation zone; cooling at least a substantial part of said secondary extract phase and pumping said cooled secondary extract phase into said first fractionation zone to serve as solvent therein.

10. In the refining of a fatty oil by a series of at least two paracritical fractionations with a low-boiling solvent having a critical temperature not substantially higher than 450° F., the improvement which includes the steps of: subjecting said fatty oil to a first fractionation into primary extract and raffinate phases in a first fractionation zone with a solvent comprised principally of said low-boiling solvent under temperatures in the paracritical range and under liquefying pressure; separately withdrawing said primary extract and raffinate phases and subjecting at least part of said primary extract to a subsequent fractionation into secondary extract and raffinate phases in a separate fractionation zone with additional solvent, said solvent being comprised principally of said low-boiling solvent, and said subsequent fractionation being carried out at a pressure sufficient to maintain said solvent-oil mixture in liquid condition but substantially lower than the pressure prevailing in said first fractionation zone; separately withdrawing said secondary extract and raffinate phases from said separate fractionation zone; and pumping at least a substantial part of said secondary extract

phase into said first fractionation zone to serve as solvent therein.

11. In the refining of a fatty oil by a series of at least two paracritical fractionations with a low-boiling solvent having a critical temperature not substantially higher than 450° F., each of said fractionations being carried out in a vertically extended fractionation zone with an extract phase outlet at the upper end, a raffinate phase outlet and solvent inlet near the lower end, and a charge oil inlet intermediate said ends, the improvement which includes the steps of: charging said fatty oil and a solvent comprised principally of said low-boiling solvent to a first vertically extended fractionation zone and regulating the conditions of temperature and pressure therein to form a primary extract phase containing a major proportion of said fatty oil and a primary raffinate phase containing a minor proportion of said fatty oil including a concentration of color bodies of said oil; separately withdrawing said extract and raffinate phases from said extract and raffinate phase outlets respectively and charging to a second vertically extended fractionation zone a charge derived from said primary extract phase; countercurrently contacting said charge with said low-boiling solvent in said second zone and regulating the conditions of temperature and pressure therein to reject a major proportion of the oil in said charge into a secondary raffinate phase and to form an upflowing extract phase containing a relatively small proportion of oil; separately withdrawing said secondary extract and raffinate phases from said second fractionation zone; diverting at least a major proportion of said secondary extract phase and adjusting the temperature and pressure of said diverted portion to a condition of greater solubility of said low-boiling solvent and said fatty oil; and introducing said diverted portion into the lower portion of said primary fractionation zone to supply thereto at least a major portion of solvent required in said zone.

12. A method as described in claim 11 in which the maximum temperature in the second vertically extended fractionation zone is substantially higher than the maximum temperature in the first fractionation zone and in which the diverted portion of the secondary extract phase is cooled to a temperature not higher than the lower of said temperatures.

13. A method as described in claim 11 in which said primary extract phase is treated to separate solvent therefrom and a relatively solvent-free primary extract oil comprises the charge in said secondary vertically extended fractionation zone.

14. A method as described in claim 11 in which said primary extract phase is separated into light and heavy components by heating to a higher temperature within the paracritical range and said components are charged to said second vertically extended fractionation zone at vertically spaced inlets, the light component being introduced at the higher inlet.

15. A method as described in claim 11 in which said diverted portion of said secondary extract phase is pumped into the lower portion of said first fractionation zone at a rate which is varied to permit the constant removal of a desired quantity of product from the undiverted portion of said secondary extract phase.

16. A method as described in claim 11 in which the upflowing solvent in said first vertically extended fractionation zone is comprised in part

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of said low-boiling solvent of said solvent inlet at said lower end of first fractionation zone; and in part of said diverted portion of said secondary extract phase introduced into said first zone through an inlet located substantially above said solvent inlet but below said fatty oil inlet.

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