

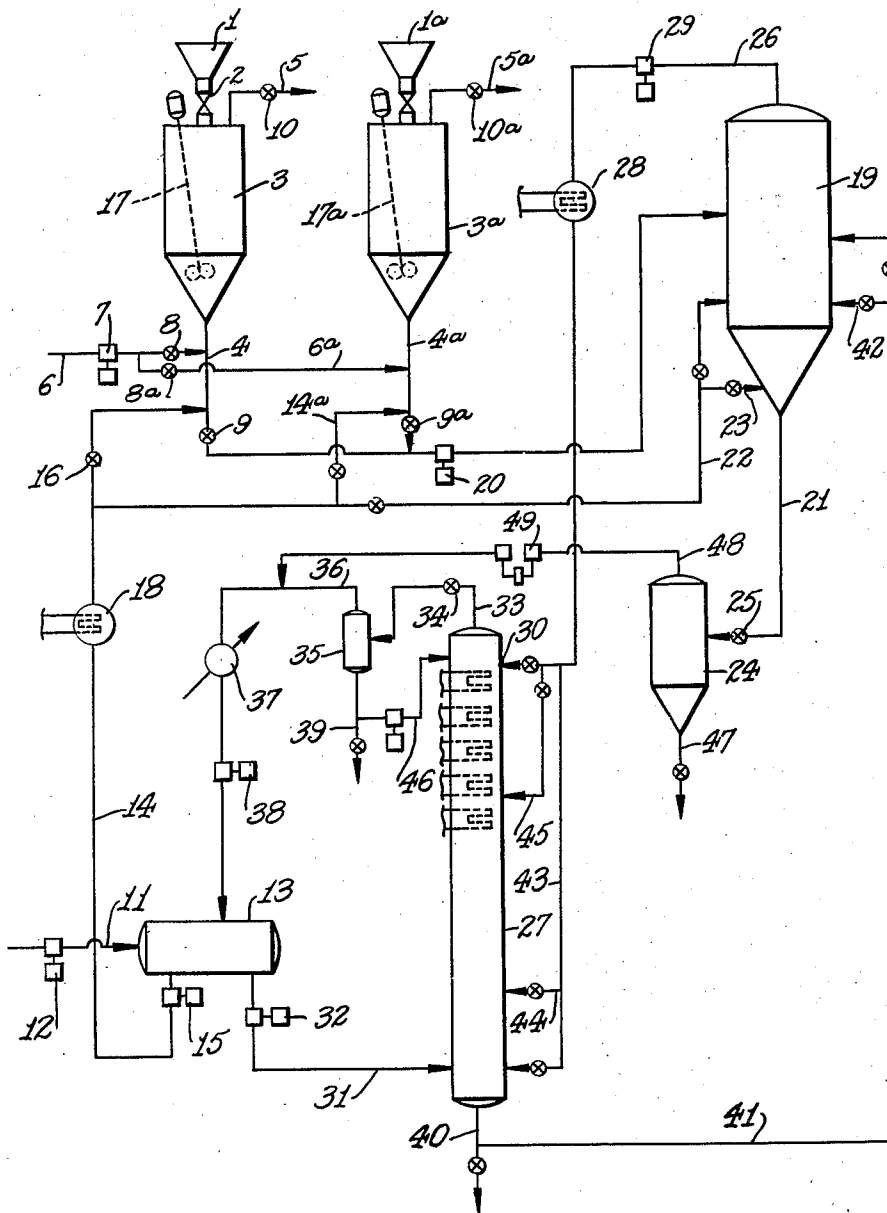
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EXTRACTION OF OLEIFEROUS MATERIALS

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EXTRACTION OF OLEIFEROUS MATERIALS

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This invention relates to an improved method for recovering fatty materials, and similar high molecular weight materials, from the solid materials with which they are normally associated in nature. Such solid materials are referred to hereinafter as "oleiferous solid materials." Such oleiferous materials include various oil-bearing beans, seeds and nuts, designated generally as oil seeds, and including soybeans, cottonseed, linseed, peanuts, palm nuts and coconuts. Other oil-bearing solid materials of animal, vegetable and marine origin also are included within the term oleiferous solid materials, such as animal tissue, including fish livers, vegetable fibers, nut shells, etc.

The invention relates particularly to an improved process of extracting oleiferous materials with relatively low-boiling solvents. Such solvents may be defined as those whose critical temperature is not substantially higher than 450° F. and preferably are lower than 325° F. Of these, the solvents which are normally gaseous are preferred because of the relative ease with which they may be separated from the oil and the residual solid material.

The low-boiling hydrocarbons represent a desirable class of solvents because of their relative inertness and low cost. While the low-boiling olefin hydrocarbons may be employed they are less desirable than the low-boiling paraffins such as ethane, propane, the butanes, the pentanes and the hexanes, from the point of view of inertness. Of the paraffins, propane is preferred ordinarily because of the high degree of solubility of the oils in that solvent and its relatively low critical temperature which permits operating in a temperature range not injurious to the oils. However, ethane or the butanes can be employed to almost as great advantage. While relatively pure hydrocarbons are preferred mixtures of them may be employed. For example, mixtures of ethane and propane or mixtures of butane and methane may be employed in the proportions suitable to form solvents having the desired properties. While the normally gaseous hydrocarbons are particularly advantageous for use as solvents in the improved method other solvents having relatively low critical temperatures may be employed, such as ammonia, dichlorodifluoromethane, dimethyl ether, methyl fluoride and halogenated hydrocarbons in general.

In accordance with the present invention the oleiferous solid materials are contacted with the liquefied solvent at a temperature effective to dissolve as much of the oil as is desired. Or-

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dinarily the temperature is maintained at a level effective to extract from the oleiferous solids the maximum quantity of the oil which can be dissolved in the amount of solvent available. Ordinarily also the solvent is employed in a sufficiently great quantity to extract from the oleiferous solids the maximum possible amount of oil.

The temperature employed for the extraction step depends upon the solvent employed and the nature of the oil to be extracted from the solid. While there is a temperature, or narrow range of temperatures, at which the solubility of the oil in the solvent is at a maximum, it is possible ordinarily to extract substantially all the oil from the solid over a relatively wide range of temperatures, when employing a sufficient quantity of solvent. For example, with propane the solvent extraction step may be carried out at temperatures within the range of from room temperature to approximately 140° F., to obtain maximum extraction of oil, although higher and lower temperatures may be employed if the propane:oil ratio is sufficiently high.

The oleiferous solids, such as oil seeds, contain a substantial proportion of relatively fine non-oleaginous solid material which is not readily separable from the extract solution by mere settling, particularly if the seeds are preliminarily flaked. Furthermore, in order to enhance the extraction of oil the oil seeds may be subjected to a preliminary fine grinding treatment which increases the proportion of fines. The bulk of the residual non-oleaginous solid materials, consisting of relatively large particles, is readily separable from the extract solution, as by mere settling, but the suspended fines which are not readily separable present a serious problem in connection with filtration, particularly if it is desired to carry out filtration on a continuous basis. In accordance with the improved process the extract solution, after separating the solids which are readily separable, is heated to a temperature above the temperature, or range of temperatures, of maximum solubility, and to a temperature near the critical temperature of the solvent, to precipitate a portion of the dissolved oil as a separate liquid phase. The formation of the separate liquid phase occludes within the relatively heavy droplets of oil the fine particles of solid material carried in suspension in the extract solution. The separate liquid phase is readily settled out of the extract solution by gravity, since the precipitated liquid phase is substantially heavier than the extract solution. In this man-

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ner the suspended fines are substantially completely separated from the extract solution which may be separately withdrawn for recovery of the extract oil.

The invention will be described further with reference to the use of propane as the solvent, but it will be understood that the principles of operation are the same in the use of any of the preferred solvents mentioned above, the operating conditions being changed only in accordance with the character of the oil to be extracted and the critical temperature of the solvent.

In its simplest embodiment the propane solution of the oil, after a preliminary separation of the readily separable solids, as by settling, is simply heated to a temperature sufficiently high to precipitate enough of the dissolved oil to occlude the suspended finely divided solids. The propane solution may be heated to the precipitation temperature in the upper part of a zone in which the bulk of the solids are settled, or the propane solution may be withdrawn from the preliminary separation zone and heated before or after introduction into a separate settling zone. According to a preferred modification of the invention, which will be described below in more detail, the propane solution is separated from the readily separable solid materials in a preliminary settling zone and passed as a stream upwardly through a second settling zone in which the stream is heated through a range of temperatures above the temperature of maximum solubility and near the critical temperature of the solvent to effect precipitation of a separate liquid phase, containing the fines, which flows downwardly through the tower in countercurrent contact with the upflowing propane solution.

The accompanying drawing presents diagrammatically an arrangement of apparatus for carrying out the improved process, and the invention will be described further by reference to the drawing, it being understood that the methods shown in the drawing are merely illustrative of the improved process.

Referring to the drawing, oleiferous material, such as oil seeds, which has, preferably, been ground to a relatively fine state of subdivision, is supplied from hopper 1 through valve 2 to extractor 3. Extractor 3 is a relatively large vessel adapted to function on a batch basis, and is provided with a bottom slurry outlet line 4 and an upper gas outlet line 5. After the desired quantity of oleiferous material is introduced into extractor 3, valve 2 is closed and a purging gas, such as nitrogen or flue gas, is introduced into outlet line 4 from supply line 6 which is provided with a compressor 7 and a valve 8. Valve 9 in line 4 is kept closed and valve 10 in line 5 is kept open during the purging operation whereby the purging gas flows upwardly through extractor 3 and the mass of oleiferous material therein to purge the chamber of oxygen from the air introduced into the chamber along with the oleiferous material. After extractor 3 has been substantially completely purged of oxygen, valve 10 is closed, the flow of inert gas is stopped, and valve 8 is closed. Optionally, the flow of inert gas into extractor 3 may be continued to build up the pressure of that vessel to the level of any superatmospheric pressure desired during the extraction step. Alternatively, the source of supply of propane may be employed to build up the pressure in extractor 3 to the necessary superatmospheric level.

Liquefied propane for use in the system is in-

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troduced through line 11, which is provided with a pump 12 and connects with a propane storage tank 13. From tank 13 liquefied propane is transferred to extractor 3 through line 14 which is provided with a pump 15 and a valve 16, and connects with line 4 between extractor 3 and valve 9. After extractor 3 has been purged and valves 8 and 10 are closed, liquefied propane is pumped into extractor 3 through lines 14 and 4 until the required quantity of propane for the extraction treatment of the oleiferous material has been supplied to extractor 3. Thereafter the supply of propane is cut off. Stirring means 17 are provided in extractor 3 to intimately mix the oleiferous material and the liquefied propane and promote extraction of oil by the propane.

The temperature in extractor 3 may be maintained at any desired level by suitable control of the temperature of the propane. For this purpose heating or cooling means 18 may be provided in line 14. In a preferred method of operation of the improved process the temperature maintained in extractor 3 is selected to produce maximum extraction of the oil by the propane. For this purpose temperatures within the range of atmospheric temperature to 140° F. may be employed, although higher or lower temperatures may be desired to produce special effects, such as the partial extraction of the oil content of the oleiferous material.

After a suitable residence time in the extractor, the slurry of propane solution and residual solid material is transferred to a vertically elongated settling tank 19. Line 4 connects with tank 19 and is provided with a pump 20. Valve 9 is opened and by means of pump 20 the slurry is pumped continuously into settling tank 19 at an intermediate point, as indicated in the drawing. Tank 19 is sufficiently large in relation to the quantity of liquids charged thereto to facilitate the settling of the larger particles of the solid material from which the oil has been largely removed.

Tank 19 preferably is operated on a continuous basis by the provision of one or more additional extractors in which a supply of the slurry of propane solution and solids is formed during the time slurry is being transferred from extractor 3 to settling tank 19. Such an additional extractor is indicated at 3a, which is substantially identical in arrangement and operation with extractor 3, and in connection with which similar parts are indicated by corresponding numerals with the subscript "a".

The solid material separated by settling in tank 19 accumulates in the bottom of the tank and is withdrawn therefrom through line 21. Propane is supplied for washing the settled material at low points in tank 19 through lines 22 and 23, which draw upon the supply of propane in line 14. The propane introduced through lines 22 and 23 removes propane solution which is entrained by the solid material by washing and dilution and provides a liquid vehicle for the removal of the solid materials as a slurry through line 21. The slurry is transferred to a separating zone in vessel 24 with which line 21 connects at an intermediate point. A valve 25 is provided in line 21 to effect reduction of pressure on the slurry. This assists in the vaporization of the propane and provides a pressure differential for transferring the slurry.

The propane-oil solution, containing suspended finely divided solid material not readily settled in tank 19, is withdrawn overhead through line

26 which connects with tower 27, which may be designated as a secondary settling zone. In accordance with one modification, the propane solution being transferred through line 26 is heated at 28 to a substantially higher temperature to effect precipitation in line 26 of a separate oil phase which occludes the suspended solids. A pump 29 is provided in line 26 to transfer the propane solution against the higher pressure which may be necessary at the elevated temperature of precipitation. In this modification the mixture of liquid phases produced as a result of heating at 28 is introduced at a high point in tower 27 by connecting line 26 with tower 27 at a point near the top, indicated at 33. In this modification tower 27 functions as a vertically elongated settling zone to permit complete separation of the liquid phases. Propane may be supplied to the bottom of tower 27 from line 31, which is provided with a pump 32 and connects with propane supply tank 13. The propane introduced into the bottom of tower 27 flows upwardly and serves to scrub the oil phase which is flowing downwardly therein and redissolve the more soluble portions thereof and leave a final lower phase containing the fines. The propane stream combines with the propane solution introduced into tower 27 from line 26 and the mixture passes overhead from the tower through line 33. Pressure on the solution is released at valve 34 and the resulting partially vaporized mixture is introduced into a separator 35 in which vaporized propane is separated and withdrawn overhead through line 36. Line 36 is provided with cooling means 37 for condensing the propane and a pump 38 for transferring the liquefied propane into supply tank 13, with which line 36 is connected. Heating means, not shown, may be supplied in separator 35 to assist vaporization of propane. The resulting oil, substantially completely free of suspended solids, is withdrawn from separator 35 through line 39. This material may not be completely free of propane and may require further treatment to remove such residual quantities of the solvent, such as steam stripping.

The oil phase separated from the propane solution by precipitation, and containing the fines, flows to the bottom of tower 27 and is withdrawn as a liquid stream through line 40. This material may be withdrawn entirely from the system, but preferably is recycled, at least in part, to the settling step of the extraction procedure to redissolve the oil in the propane solution and incorporate the fines in the residual solids withdrawn from the bottom of settling tank 19. For this purpose line 41 is provided to connect line 40 with tank 19 at a mid point thereof. Alternatively, the oil phase returned through line 41 may be introduced at a relatively low point in tank 19, as by connection at 42, in order to utilize the downwardly moving mass of solids to assist in trapping fines contained in the recycled oil. If tower 27 is employed to concentrate the color bodies in the oil, according to a modification described below, a portion of the bottoms from tower 27 may be withdrawn from the system while another portion is recycled through line 41.

In accordance with another modification of the invention, the propane solution from line 26 is introduced at a point near the bottom of tower 27, in the substantial absence of propane from any other source in tower 27. For this purpose line 43 is provided to connect line 26 with tower 27 at a low point. In this modification the propane solution is heated at most only partially

at 28 and is heated to the final desired high temperature as it flows up the tower toward the exit at 33. For heating the propane solution in tower 27 heating coils indicated diagrammatically in the drawing are provided along the length of tower 27, principally in the upper portion thereof, to heat the propane solution gradually to the final desired high temperature. In this manner precipitation of the lower phase occurs all along the length of the path in which the stream is heated whereby the occlusion of fines in the droplets formed by precipitation is enhanced. The precipitate formed in tower 27 flows down the tower and is subjected to countercurrent contact with the upflowing propane solution. By this means the oil is fractionated to a greater degree and the concentration of less soluble components in the lower phase is increased. To enhance this effect the propane solution may be introduced at a point somewhat removed from the bottom of tower 27 as through line 44, while additional propane is introduced at the bottom through line 31. Additional propane serves to scrub the lower phase for the recovery of more soluble components thereof prior to withdrawal of the lower phase from tower 27 through line 40. To enhance the scrubbing action of the additional propane the propane solution may be introduced at a point near the middle of tower 27, as through line 45. To intensify the rectification of the tower, produced by the precipitation of the lower phase, and produce closer fractionation of the oil, a portion of the extract oil recovered overhead at 35 may be returned through line 46 to the upper portion of tower 27. Tower 27 may be provided with trays or packing to enhance contact of the liquid phases.

The proportion of the oil which is precipitated from the propane solution to effect removal of fines may vary from 1 to 20 percent, or higher. The oil thus precipitated is not lost from the product, as it may be recycled to the separation zone through line 41 and redissolved in the propane phase. If it is desired to utilize tower 27 as a means for concentrating color bodies of the oil in a small bottoms fraction which is to be withdrawn from the system, it is preferable to heat the propane phase to a final high temperature in tower 27 which precipitates a substantially large proportion of the oil, which is then subjected to scrubbing treatment with additional propane from line 31 in the bottom of tower 27 to reduce the volume of the lower phase, by redissolving oil, to the proportion of the oil charge which it is desired to remove from the system as the color body fraction. Ordinarily the temperatures to which the propane solution is to be heated are all within the range of 140-200° F.

The solids are withdrawn from separator 24 through line 47 in a relatively dry condition by any suitable means, such as a star feeder. The solids thus withdrawn are then subjected to further treatment, as by steam, for the removal of propane therefrom. To assist the removal of propane in separator 24 suitable heating means, such as a heating coil, not shown, may be provided in separator 24. The propane withdrawn overhead in separator 24 is transferred through line 48 to line 36 for passage back to propane storage at 13. A compressor 49 is provided in line 48 to recompress the propane to the pressure of line 36.

Instead of operating the extraction zones on a batch basis as is illustrated in the drawing, it is within the scope of the invention to contin-

uously mix the solvent and solids in a continuous extraction zone and continuously transfer the resulting mixture of propane solution and solids to settling tank 19. In this operation some of the oil may be extracted in tank 19, particularly if additional propane is introduced through lines 22 and 23.

In the foregoing description, the final separation of finely divided non-oleaginous solids by precipitation of a separate liquid phase follows a preliminary partial separation of the readily separable portion consisting of the larger particles of the solid material which has been subjected to extraction treatment. For an example of such a preliminary separation reference has been made to simple settling of such readily separable solid materials, and in the detailed description of the invention, as illustrated in the drawing, this preliminary separation step has been provided for by passing the slurry from the extraction zone to an enlarged settling vessel shown in the drawing at 19. It will be understood, however, that the invention is not limited to an operation in which the preliminary separation is effected by settling, since other methods may be employed to separate the readily separable solids prior to the final separation step. For example, instead of a settling step the slurry from the extraction zone may be passed to a filtration step in which the filtering medium is relatively coarse. The coarseness of the filtering surface prevents clogging and greatly simplifies the operation, but permits the passage of relatively fine solid materials, which are separated by precipitation of a separate liquid phase in a subsequent zone. In accordance with another method of effecting preliminary separation of the readily separable materials, the slurry from the extraction zone may be passed to a centrifugal separation apparatus on which the duty would be quite low, since it would not be necessary to separate the finest portion of the solid material. It will be understood, therefore, that in the foregoing description and in the following claims references to the preliminary separation of readily separable solids are not limited in their specific application to the settling method shown in the drawing.

The separate liquid phase which is formed by heating the extract phase is readily separated by settling, as indicated above. However, other means for effecting such separation, such as a centrifuge, are within the scope of the invention.

As stated above, the temperature at which the extraction step is carried out is maintained at the level at which the desired proportion of the oil content of the oleiferous material is dissolved in the solvent. It is within the scope of the invention to maintain the temperature of extraction at a level substantially above the temperature of maximum solubility whereby only a portion of the oil contained in the oleiferous material is dissolved in the solvent. This permits selective extraction of desired portions of the oil while leaving with the solid residue a portion of the oil which it is not desired to include in the extract. This involves conducting the extraction at temperatures substantially above the temperature levels employed in previous extraction processes and at temperatures not far below the critical temperature of the solvent. For example, when it is desired to extract only a portion of the oil in accordance with this modification the minimum temperature in the extraction zone should not be more than about 70° F. below the critical temperature of the solvent. When employing

propane as the solvent in accordance with this modification the extraction temperature should not be lower than about 140° F. Relatively high temperatures above this level are employed to extract smaller portions of the oil content of the oleiferous solids.

In carrying out the process according to the modification in which only a portion of the oil is extracted from the oleiferous solid the latter may be subjected to a plurality of successive treatments at decreasing temperature levels to extract a plurality of separate fractions of the oil or fat from the oleiferous material. For example, in a two-stage extraction treatment the oleiferous material is first extracted with the propane at a relatively high temperature, e. g., substantially above 140° F., to extract a portion of the oil which is unusually light in color and free from color bodies. In this fraction are concentrated the free fatty acids, the unsaponifiable portion of the oil or fat, and any oil-soluble vitamins present in the oil. In a second partial extraction of the oleiferous material at a somewhat lower temperature another oil fraction is obtained which is substantially free from color bodies and which is different in composition from the first oil fraction in being relatively free from fatty acids and unsaponifiable material. If the second treatment is carried out at a temperature substantially above the temperature of maximum solubility the second oil fraction also will be relatively free from color bodies. By carrying out repeated treatments at successively lower temperatures all the desired materials are finally removed, leaving only undesirable extractable materials with the solid portion of the oleiferous material. The products of such successive extraction steps represent semi-refined, or fully refined, fractions which, because of the method of production, do not require subsequent refining to the extent required by oils recovered by previous methods.

In carrying out successive extraction treatments by the method illustrated in the drawing the first treatment would be at substantially elevated temperature whereby the solids settled out in tank 19 would contain a substantial proportion of unextracted material. The slurry of such solids and propane withdrawn from tank 19 through line 21 would not be passed to a zone of lower pressure as illustrated in the drawing, but would be transferred by means of a suitable pump to a second extraction step generally similar to that illustrated in the drawing for contact with an additional supply of propane at a lower temperature.

I claim:

1. A method for recovering oil from solid oleiferous material containing oleaginous material associated with non-oleaginous material which comprises intimately contacting said oleiferous material with a solvent for the oil content thereof to form a slurry of solids in extract solution, said solvent having a critical temperature not substantially higher than 450 degrees Fahrenheit, separating readily separable coarser solid particles from said slurry leaving a suspension of solid fines in the extract solution, heating said suspension to a temperature above the temperature of maximum oil solubility and near the critical temperature of said solvent to precipitate an oil phase heavier than said extract solution and containing said solid fines in occlusion while maintaining said suspension under a pressure sufficient to prevent substantial vaporiza-

tion of said solvent, and separating said fines-containing oil phase from the remaining extract solution.

2. A method for recovering oil from solid oleiferous material containing oleaginous material associated with non-oleaginous material which comprises intimately contacting said oleiferous material with a solvent for the oil content thereof to form a slurry of solids in extract solution, said solvent having a critical temperature below 325 degrees Fahrenheit, separating readily separable coarser solid particles from said slurry leaving a suspension of solid fines in the extract solution, heating said suspension to a temperature above the temperature of maximum oil solubility and near the critical temperature of said solvent to precipitate an oil phase heavier than said extract solution and containing said solid fines in occlusion while maintaining said suspension under a pressure sufficient to prevent substantial vaporization of said solvent, and separating said fines-containing oil phase from the remaining extract solution.

3. A method according to claim 1 in which said solvent comprises a liquefied normally gaseous material.

4. A method according to claim 1 in which said solvent comprises a liquefied normally gaseous hydrocarbon.

5. A method according to claim 1 in which said oleiferous material is contacted with said solvent at a temperature effective to dissolve a maximum amount of said oleaginous material in said solvent.

6. A method for recovering oil from solid oleiferous material containing oleaginous material associated with non-oleaginous material which comprises intimately contacting said oleiferous material with a solvent for the oil content thereof to form a slurry of solids in extract solution, said solid having a critical temperature not substantially higher than 450 degrees Fahrenheit, separating a readily separable coarser portion of the solids from said slurry in a separation zone leaving a suspension of solid fines in the extract solution, heating said suspension to a temperature above the temperature of maximum oil solubility and near the critical temperature of said solvent to precipitate an oil phase heavier than said extract solution and containing said solid fines in occlusion while maintaining said suspension under a pressure sufficient to prevent substantial vaporization of said solvent, separating said fines-containing oil phase from the remaining extract solution, and returning the said fines-containing oil phase to said separation zone.

7. A method for recovering oil from solid oleiferous material containing oleaginous material associated with non-oleaginous material which comprises intimately contacting said oleiferous material with a solvent for the oil content thereof to form a slurry of solids in extract solution, said solvent having a critical temperature not substantially higher than 450 degrees Fahrenheit, separating readily separable coarser solid particles from said slurry by settling leaving a suspension of solid fines in the extract solution, heating said suspension to a temperature above the temperature of maximum oil solubility and near the critical temperature of said solvent to precipitate an oil phase heavier than said extract solution and containing said

solid fines in occlusion while maintaining said suspension under a pressure sufficient to prevent substantial vaporization of said solvent, and separating said fines-containing oil phase from the remaining extract solution.

8. A method according to claim 7 and the step of returning said fines-containing oil phase to the zone of settling of said readily separable solids.

9. In the recovery of oil from oil seeds by extraction with a solvent for the oil content thereof having a critical temperature not substantially higher than 450 degrees Fahrenheit, the improved method which comprises crushing the oil seeds, intimately contacting the crushed seeds with said solvent under liquefying pressure to form a slurry of solids in extract solution, separating readily separable coarser seed particles from said slurry leaving a suspension of solid fines in the extract solution, adjusting the temperature of said suspension to the range near the critical temperature in which the solubility of oil in the solvent decreases with increasing temperature to precipitate a relatively heavy raffinate phase in sufficient quantity to carry down said solid fines and separately withdrawing said extract solution substantially free of solid fines.

10. In the recovery of oil from seeds by extraction with a solvent for the oil content thereof having a critical temperature not substantially higher than 450 degrees Fahrenheit, the improved method which comprises intimately contacting said seeds in finely divided form with said solvent under liquefying pressure to form a slurry of solids in extract solution, separating readily separable coarser seed particles from said slurry leaving a suspension of solid fines in the extract solution, continuously introducing said suspension into a vertically extended fractionation zone through a mixture inlet located above a solvent inlet and a raffinate phase outlet and below an extract phase outlet, countercurrently contacting said suspension with additional quantities of said solvent introduced through said solvent inlet, maintaining a gradient of temperature increasing with elevation within said fractionation zone in the region between said mixture inlet and said extract phase outlet, said temperature gradient being in the range near the critical temperature in which solubility of oil in said solvent decreases with increasing temperature, adjusting said temperature gradient to precipitate from said suspension a relatively heavy raffinate phase in sufficient quantity to carry down said solid fines, and separately withdrawing extract and raffinate phases from said extract and raffinate phase outlets respectively.

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