

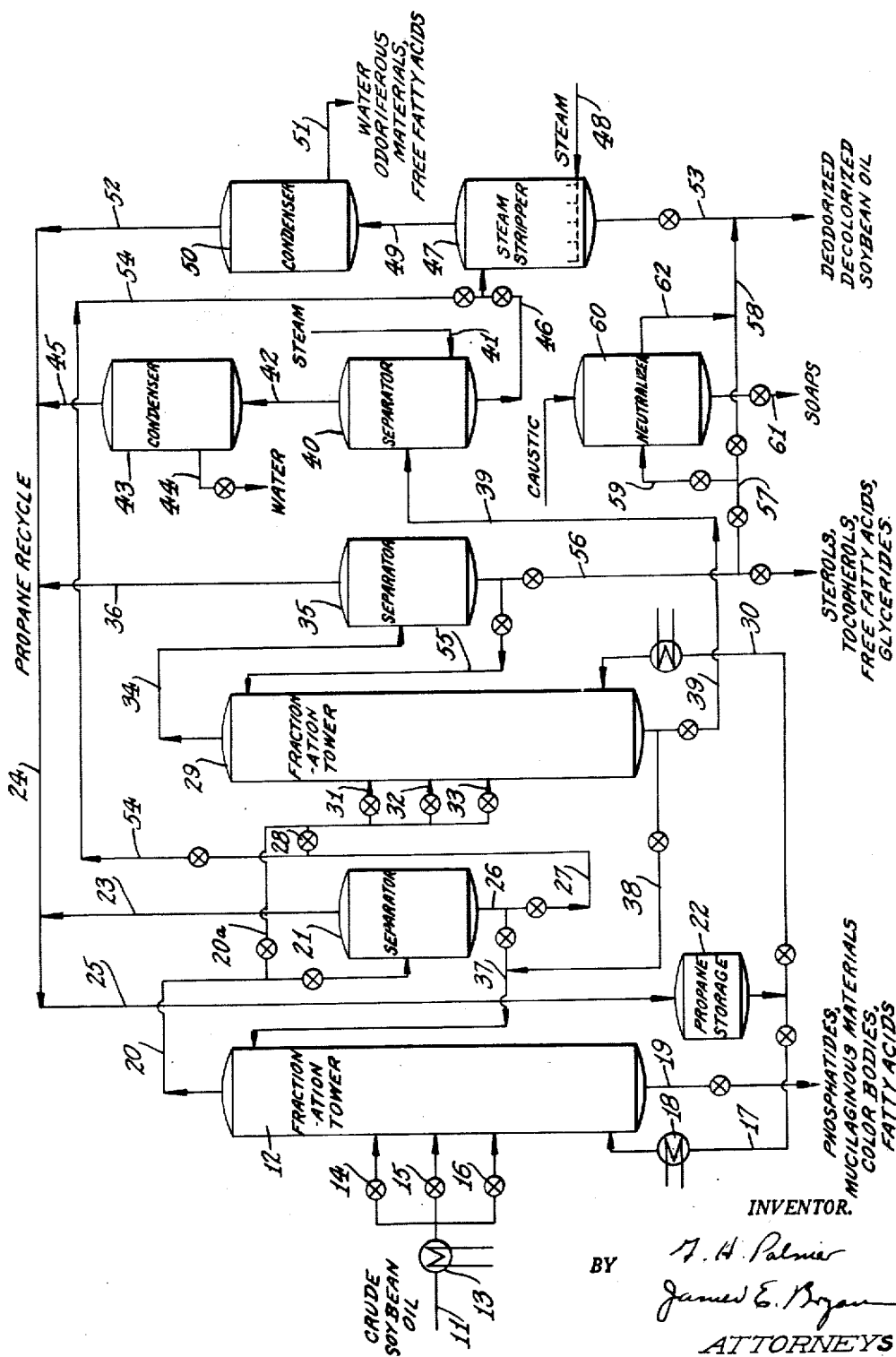
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REFINING OF SOYBEAN OIL

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REFINING OF SOYBEAN OIL

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This invention relates to an improved process for refining vegetable oils and more particularly to a process for producing colorless neutral oil without caustic treatment of the oil. The process involves removing color bodies, fatty acids and other impurities from the oil in two steps: first, eliminating color bodies and polyfunctional fatty acids or fatty acids of high molecular weight by dissolving the oil in a low boiling solvent under paracritical conditions, and second, eliminating the remaining fatty acids and more easily vaporized impurities by treatment with steam. In a preferred form of the process, the condensate from the steam treatment is neutralized and washed to remove soaps and the remaining condensate is returned to the vegetable oil to restore certain minor components which help to prevent rancidity.

This application is a continuation-in-part of copending application Serial No. 463,559, filed October 20, 1954, now abandoned, which is in turn a continuation-in-part application Serial No. 181,235, filed August 24, 1950, and now abandoned, which in turn is a continuation-in-part of application Serial No. 699,320, filed September 25, 1946, and now abandoned.

Vegetable oils such as soybean oil, cotton seed oil, linseed oil and palm oil are obtained by pressing or solvent extraction of seeds, beans or other vegetable source in which they originate. Resulting oil is treated in various ways depending upon the nature of the oil, but in almost every case, it is necessary to neutralize the oil by removal of fatty acids and to decolorize it by removal of color bodies. At present, neutralizing is accomplished by treating the oil with caustic and washing out the soaps. This step is usually accompanied by a loss of 3 to 4½ percent of the crude oil because some of the glycerides in the oil are converted into soaps along with the fatty acids. Decolorizing is ordinarily accomplished by bleaching with clay, activated carbon, or a hydrated magnesium oxide. The final bleached oil is treated with steam under vacuum in order to deodorize the oil. In the case of certain oils, such as soybean oil, the above processing must be preceded by a hydrolysis step to remove phosphatides. The total loss encountered in refining is commonly between 4 and 6 percent and sometimes even higher.

The present invention substantially reduces the cost of refining vegetable oils and, in addition, reduces the losses to less than half that encountered in present commercial refining. Principally, the savings are achieved by eliminating the neutralizing step and replacing it with two complementary steps for eliminating fatty acids. The fatty acids contained by the typical crude vegetable oil are mostly very soluble in propane as long as they exist in their simple form uncomplicated by the substitution of hydroxyl or other groups for hydrogen in the acid structure. If, however, some deterioration of the acid takes place, and there is a substitution of a hydroxyl group, ketone, or an alcohol, or some other group containing nitrogen, phosphorous, or the like, the solubility of the

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acid is radically changed, becoming very slight. Fatty acids are thus either among the most soluble or the least soluble components in the crude vegetable oil; fatty acids of intermediate solubility are too minor to be of any concern. The phenomenon, the fact that almost all of the fatty acids in a crude vegetable oil are either of the very soluble unsubstituted type or the almost insoluble polyfunctional type, makes the present invention possible. Although it has never been possible to neutralize crude vegetable oils by steam treatment because there always remained polyfunctional acids which would not vaporize out of the oil, the present process makes possible adequate commercial neutralization, that is neutralization to reduce the fatty acid content of the oil to 0.05 percent or less, without chemical neutralization, by eliminating the polyfunctional acids in a solvent fractionation, followed by steam treating to vaporize the unsubstituted fatty acids from the oil.

Although the process is applicable to almost any vegetable oil which requires neutralizing and decolorizing, its application may be conveniently illustrated by a description of the treatment of soybean oil. The crude soybean oil is first contacted with a solvent having a relatively low critical temperature, preferably under 450° F., and substantially all of the oil is dissolved in said solvent, leaving only about one or two percent of the crude oil in a dense phase. Preferably, the oil is continuously charged to a countercurrent fractionation or extraction zone. The fractionation is carried out in a temperature range between the temperature of maximum miscibility of solvent and oil and the critical temperature of the solvent-oil mixture. The temperature employed usually falls in a range of about 100° F. below the critical temperature of the solvent-oil mixture. Within this range, the miscibility of the oil and the solvent may be controlled with considerable precision because the density of the solvent, and hence its solvent power, decreases with increasing temperature (or decreasing pressure); as explained hereinafter, this phenomenon makes it possible to reject from the oil a predetermined least soluble fraction thereof. In this first step of the process, the least soluble color bodies, fatty acids, and the like are eliminated, in a bottom fraction amounting to between about 1.5 and 5 percent of the oil, usually in a fraction of less than 2 percent. These least soluble materials are also the materials which have relatively high molecular weight and high boiling point. Although most of the color bodies are thus eliminated, a few coloring materials of low molecular weight and high solubility remain. Furthermore, the lighter weight fatty acids remain. A second step is therefore necessary to remove the impurities which could not be rejected in the solvent treatment. The low molecular weight, low boiling point impurities are eliminated by subjecting the extract oil (preferably after the removal of all or most of the solvents) to treatment under vacuum with steam. It will be seen from this brief description that the invention broadly comprehends two steps: first, the rejection of relatively heavy impurities by solvent treatment and second, the elimination of the relatively low molecular impurities by evaporating them with steam. In another preferred form of the invention these two steps are augmented by a second solvent treatment step. In one mode of practicing the invention, the extract phase from the solvent treatment is subjected to a second solvent treatment at higher temperature or lower pressure or both so as to precipitate substantially all of the oil, leaving only about 0.5 to 15 percent, preferably about 1 percent, in the extract phase; the small overhead is only sufficiently large to carry with it substantially all the remaining fatty acids and other undesired impurities.

Although the condensate from the steam treatment is ordinarily comprised of at least 50 percent fatty acids,

which are in no way desirable in the refined oil, it also contains certain complex substances which are present only as traces in the raw oil but serve an important function, that of enabling the raw oil to resist rancidity. It has been found that the deodorized oil is less stable and will go rancid faster than raw oil, but that the stability of the oil can be substantially restored by restoration of the condensate residue left after removal of fatty acids. It is a preferred species of the present invention to neutralize the condensate, wash out soaps which are formed and restore the neutral condensate residue to the refined oil.

The oil from the fractionation zone may, if desired, be partially or entirely treated in a second countercurrent fractionation zone with the same or a similar solvent for the purpose of removing a small fraction containing the sterols, tocopherols, as well as some of the free fatty acids and a small portion of the glycerides.

It will be seen from the above brief description of the present process that only two steps are required to obtain an oil having all the desirable characteristics for use in either the paint industry or in the food industry. In the past it has always been necessary to treat the crude soybean oil with caustic in order to remove the free fatty acids. The treatment with caustic not only involves considerable losses, based on the crude oil, but also involves considerable difficulty in the removal of the soaps from the oil as well as the removal of occluded oil from the soaps. Furthermore, the method involving the treatment with caustic invariably results in the saponification of some of the glycerides, thereby increasing the losses. In addition, the caustic causes various chemical reactions to occur in the oil which produce undesired results. The present process avoids all of the disadvantages of treating the oil with caustic since the oil is at no time treated with chemicals of any kind. All of the undesirable materials are eliminated from the crude soybean oil by countercurrent contact with a solvent in a fractionation zone. According to the present process, the refining losses are reduced to less than one half of those previously encountered so that the total yield of deodorized, decolorized, refined soybean oil amounts to about 97 percent or higher.

The solvents having the desired characteristics are normally gaseous and must be used under such conditions of liquefying pressure that the required degree of solvency for the soybean oil is obtained. The solvent, in the liquid state, and the soybean oil are continuously contacted preferably in a countercurrent fractionation zone under such conditions of temperature and pressure that two homogeneous mixtures or phases having different densities are obtained. The upper or lighter phase consists principally of the solvent and the desired portion of the oil while the lower or heavier phase consists of the undesired phosphatides, color bodies, polyfunctional fatty acids and mucilaginous material and a very small portion of the solvent. The solvents, which may be used for the present process, must exhibit the characteristic of having decreased solvent power for various components of the oil as the temperature is increased. In addition, the range of temperatures employed must be substantially below those temperatures at which any thermal decomposition or chemical reaction occurs in the soybean oil. Preferably the solvent should have a critical temperature well below the decomposition temperature of the soybean oil, i. e., not substantially higher than 450° F. and preferably below 325° F. The miscibility of the soybean oil and such solvents decreases with increases in temperature in the paracritical range between that temperature at which there is substantially complete miscibility of the solvent and soybean oil, i. e., about 100° F. below the critical temperature and a higher temperature not substantially greater than the critical temperature of the solvent. At the higher temperature, the soybean oil and solvent are substantially immiscible.

The low molecular weight hydrocarbons are particu-

larly suitable for use in the present process since they exhibit the above necessary characteristics. The low molecular weight paraffin hydrocarbons are especially useful since they are inert to substantially all components of the soybean oil. The low boiling, normally gaseous and normally liquid paraffin hydrocarbons such as methane, ethane, propane, the butanes and the pentanes are, therefore, preferred as solvents, but it has also been found that the corresponding olefin hydrocarbons may be used with satisfactory results and these latter compounds are, therefore, not excluded. Since propane exhibits all of the desired characteristics to a higher degree than some of the other solvents mentioned, it is the preferred solvent for the present process. Furthermore, mixtures of any two or more of the above-mentioned hydrocarbon solvents may be used as well as the relatively pure compounds. In addition to those solvents previously mentioned, other solvents having relatively low critical temperature may also be employed, such as ammonia, ethylene oxide, dimethyl ether and methylamine and halogenated hydrocarbons such as dichlorodifluoromethane.

According to the present process the solvent and the desired portion of the oil is taken overhead from the countercurrent fractionation zone while the less desirable portion, i. e., the phosphatides, mucilaginous materials, as well as some of the color bodies and fatty acids, is removed from the bottom of said zone. If desired, the overhead fraction may be treated similarly in order to remove an overhead fraction containing some of the unsaponifiable materials including the sterols and tocopherols, as well as some of the free fatty acids and a minor portion of the glycerides. The material withdrawn from the bottom of said second fractionation zone or the overhead fraction from the first fractionation zone may be treated with steam under vacuum to remove odor forming materials, whatever free fatty acids remain and at the same time effect a striking decolorization of the soybean oil, which will be discussed further hereinafter. If desired, intermediate fractions for special purposes may be removed from either of the countercurrent extraction zones.

The accompanying drawing illustrates a flow sheet of a system for treating crude soybean oil according to the present invention. The drawing illustrates all of the essential features of the system schematically, but does not include various mechanical details which are well known to those skilled in the art.

Crude soybean oil which has been expressed or extracted from the soybeans is introduced through line 11 to fractionation tower 12. In order that the temperature of the soybean oil may be raised to the desired level, a heater 13 is provided in line 11. The oil may be introduced through any one or more of valved lines 14, 15, and 16 disposed intermediate the ends of the fractionation tower 12. Propane is introduced near the bottom of tower 12 through line 17 which may be provided with a heater 18 to raise the temperature to the desired level. When the crude soybean oil is introduced into the fractionating tower at an intermediate point thereof, the lower portion of said tower will operate as an absorption or stripping zone while the upper portion, above the point of introduction of the oil, will serve as a rectification zone as will be described more fully hereinafter. As the propane rises through the tower 12 from its point of introduction thereto, and the oil descends therethrough, a countercurrent extraction of the soybean oil is effected and those components of the oil, such as the phosphatides, the mucilaginous materials as well as some of the color bodies and fatty acids, which are insoluble or immiscible with the propane, at the conditions employed, will flow to the bottom of tower 12 where they may be withdrawn from the system through valved-line 19.

The overhead from tower 12 may be passed through line 20 to separator 21 where the propane solvent may be separated from the dissolved fatty materials by evapora-

tion or the like. The separated propane may be returned to the storage tank 22 through lines 23, 24, and 25. The overhead from tower 12 consists essentially of propane solvent having dissolved therein the oily material and glycerides which are contained in the soybean oil. Since a substantial amount of the undesirable materials have been removed from the overhead fraction, the oily material which is removed from the bottom of separator 21 through line 26 has a lighter color than the original oil. In order to remove further color bodies or pigments from the oil, and in order to improve its odor characteristics, the oil may be passed through lines 27 and 28 to a second fractionation tower 29. Additional propane may be introduced near the bottom of tower 29 through line 30 in a manner similar to that described in connection with tower 12. The fractionated oil from separator 21 may be introduced into the second tower 29 through one or more of valved-lines 31, 32, and 33 at points intermediate the ends of said tower. However, the conditions of temperature and pressure in fractionation tower 29 are maintained so that a small overhead fraction is obtained which contains most of the unsaponifiable materials such as the sterols and tocopherols as well as free fatty acids and a minor proportion of the glycerides. This overhead is withdrawn from tower 29 through line 34 and is passed to a separator 35 for removal of propane contained therein. The removed propane may be returned to storage tank 22 through lines 36, 24, and 25.

When it is desired to pass all of the overhead from fractionation tower 12 to the fractionation tower 29, it will be advantageous to circumvent separator 21 by passing all of the overhead from tower 12 through lines 20 and 20a directly into tower 29 through one or more of lines 31, 32, and 33. Or if desired, a portion of the overhead from fractionation tower 12 may be introduced into the separator 21 for removal of solvent therefrom and the remaining portion of the overhead may be bypassed through line 20a directly to the fractionation tower 29.

It will be clear that when the overhead from tower 12 is passed directly to tower 29 without the intermediate removal of propane in separator 21, the quantity of propane to be introduced into the bottom of fractionation tower 29 through line 30 need only be sufficient to make up to the desired propane-soybean oil ratio. On the other hand, it is possible that less propane will be necessary for effecting the desired separation in fractionation tower 29 than is present in the overhead stream from fractionation tower 12 and, in this case, the desired ratio of propane to soybean oil may be obtained by passing a portion or all of the overhead from tower 12 through the separator 21 to remove only the undesired portion of the propane therefrom and subsequently passing the remaining material from the bottom of separator 21 through lines 26, 27, and 28 to fractionation tower 29.

If desired, a portion of the material withdrawn through line 26 from the bottom of separator 21 may be returned to tower 12 for refluxing by passing it through line 37. Also, if desired, a portion of the material withdrawn from the bottom of tower 29 may be passed through line 38 into line 37 for refluxing as will be described more fully hereinafter. The oil which is withdrawn from the bottom of tower 29 is normally passed through line 39 to separator 40 for removal of any propane which has been dissolved in the oil. If desired, the propane may be removed in separator 40 by introducing steam through line 41 to assist vaporization of the propane. In this instance, the vapors withdrawn from the top of separator 40 through line 42 are passed to a condenser 43 where the steam is condensed and water withdrawn through line 44. The propane is passed overhead through line 45 to line 24 and thence to storage tank 22 through line 25. The depropanized oil is passed from the bottom of separator 40 through line 46 to a point near the top of stripping tower 47. Steam is introduced into the bottom of said stripping tower 47 through line 48 and passes upwardly

through the column of oil introduced at the top thereof. The overhead from the stripping column 47 consists of steam accompanied by any free fatty acids which might still remain in the oil as well as odoriferous materials. This mixture is passed through line 49 to a condenser 50 where the water, fatty acids, and odoriferous materials are condensed and withdrawn through line 51. Any propane which might have accompanied the overhead from the stripper tower 47 is returned to the system through lines 52, 24, and 25 to the propane storage tank 22. The refined soybean oil is withdrawn from stripper 47 through line 53.

There is evidence to indicate that the tocopherols and possibly other materials function in the nature of inhibitors against color and taste reversion in the refined soybean oil, and it is, therefore, at times desirable to leave some or all of the tocopherols as well as some of the sterols in the finished oil. To accomplish this the small overhead fraction, which contains the sterols, tocopherols, as well as some of the free fatty acids and glycerides, is not removed from tower 29 but rather the overhead from fractionation tower 12 is first passed to separator 21 through line 20 for recovery of the propane, and the bottoms from separator 21 are then passed through lines 27 and 54 for introduction directly into the stripper column 47. However, since the tocopherols have a rather high pharmaceutical value, it is sometimes advantageous to remove at least a part of the tocopherols and sterols for separate treatment. If it is desired to remove some of the sterols and tocopherols, but at the same time, retain a small percentage thereof in the finished oil, this may be accomplished, for example, by passing the soybean oil through fractionation tower 12, separator 21 then through fractionation tower 29 and separator 35. A part of the bottoms from separator 35 may be returned to tower 29 through line 55 for refluxing. The remainder of the bottoms from separator 35 may be withdrawn from the system through line 56 for further treatment as stated hereinbefore, or a part or all of the bottoms may be added to the finished oil by passing the same through lines 57 and 58 to line 53. On the other hand, if it is desired to remove any free fatty acids which might be contained in this fraction of the oil, it may be passed through lines 57 and 59 to a neutralizer 60 for treatment with caustic so that the fatty acids can be removed as soaps through line 61. The remaining material consists largely of the sterols and tocopherols and is withdrawn from the neutralizer 60 through line 62 and is added to the finished oil in line 53 for inhibiting odor and taste reversion.

It will be noted that the propane solvent is continuously recycled through the system. It passes first from storage tank 22 through lines 17 or 30 to the fractionation towers 12 or 29 respectively. The overhead from each of the separators 21 and 35 and condensers 43 and 50 is returned through lines 23, 36, 45, and 52 to line 24 and then to line 25 and the storage tank 22.

It will be understood that the various methods for recovering the propane from the various fractions may be carried out by any of the well known methods. This may be accomplished by heating the overhead material to cause evaporation of the propane which is subsequently condensed, or the fractions may be heated to a point near the critical temperature of the propane to cause a phase separation between substantially all of the fatty material and the propane. In addition to these methods, the propane may be removed from the overhead products by steam stripping with subsequent condensation for the removal of water from the propane-steam mixture. Furthermore, if desired, a combination of two or more of the foregoing methods for recovery of the propane may be used.

When crude soybean oil is introduced through line 11 to the fractionating tower 12, a maximum temperature is maintained at the top of the tower and a minimum temperature at the bottom of said tower. The bottom temperature may be conveniently controlled by the tem-

perature of the propane being introduced through line 17. The soybean oil, which is introduced through line 11, may be heated to the same temperature as that of the propane, so that the temperature between the soybean oil and propane charge points is substantially uniform, or if desired, the soybean oil may have a higher temperature than the propane so that there will be temperature gradient between the charge points.

The lower portion of the fractionating tower 12, below the charge point of the soybean oil, functions primarily as an absorption zone in which the components of the soybean oil which are not absorbed or dissolved by the upwardly flowing propane stream, flow downwardly through the tower by reason of their greater gravity. As the fatty material flows downwardly, it contacts propane which is less saturated with respect to the fatty material, so that more of this material is eventually absorbed or dissolved in the propane phase. The unabsorbed or undissolved material, such as the phosphatides, mucilaginous materials, color bodies and fatty acids, is collected at the bottom of the fractionating tower 12 and is withdrawn through line 19. The interface between the propane phase containing dissolved fatty material, and the undissolved phase may be maintained above or below the propane charge point. However, in order to obtain a better stripping effect on the undissolved phase, this interface should be located above the propane charge point.

As the propane phase containing dissolved fatty material rises upwardly through the tower above the oil charge point, it may be progressively heated to slightly higher temperatures by means of heating coils (not shown) of any conventional type. As this phase moves upwardly through the upper portion of the tower, those portions of the fatty material which become less soluble and which are undesired in the final product, are precipitated as a separate and heavier phase, containing substantially less propane than the propane-fatty material phase. This precipitated material flows downwardly from the point of precipitation in countercurrent contact with the upwardly flowing propane phase and passes from a higher temperature to a zone of lower temperature at which the capacity of the propane phase to absorb the oil is greater than at the temperature at which the precipitated material was precipitated. Therefore, the propane phase ends to reabsorb oil which has been precipitated from the propane phase at a higher temperature and at a higher point in the fractionation tower 12. It will be seen, therefore, that a highly efficient rectification of the fatty material is obtained and that the precipitated material constitutes a highly efficient refluxing in the upper portion of the tower.

If desired, refluxing by precipitation as described above, may be used instead of refluxing by introducing a portion of the product through line 37 to a point near the top of tower 12. Or if desired, both types of refluxing may be used. The degree of efficiency in the removal of undesirable constituents from the crude soybean oil is largely dependent upon the efficiency of refluxing and it is, therefore, usually desirable to utilize the most efficient refluxing in order to obtain a highly refined deodorized and decolorized soybean oil without excessive losses.

In order to improve the refluxing in tower 12, it may be sometimes found desirable to pass a portion of the bottoms from tower 29 through line 38 and line 37 to the top of tower 12. This modification will enrich the material at the top of tower 12 with the desired components of the soybean oil and will, therefore, tend to decrease the solvent power of the propane for various undesired components which might, except for the refluxing, tend to be carried overhead with the desired products through line 20.

The maximum temperature generally employed at the top of tower 12 may be higher than the critical temperature of the propane or other solvent, but it is ordinarily

preferred to operate at temperatures below the critical temperature and falling within the range of temperature between the critical temperature and 50° F. below said critical temperature. Within this range of temperatures, the lower temperatures are employed at the top of the tower when it is desired to obtain an overhead fraction containing a relatively greater proportion of the crude soybean oil, whereas higher temperatures within this range are employed when relatively smaller proportions of highly refined soybean oil are desired. In the latter case, the overhead product will have a very high degree of purity since all of the impurities will be removed from the bottom of the tower. It will, therefore, be seen that the particular temperatures involved, especially at the top of the fractionating tower 12, have considerable effect on the amount of refined soybean oil to be finally recovered and in general, greater refinement is obtained when the amount of the overhead product is reduced.

Another factor which affects the degree of refinement to a great extent is the relative quantities of crude soybean oil and propane which are introduced into the fractionating tower 12. Considerable refinement is obtained when the propane to soybean oil ratio is about 5:1 by volume. However, far better refinement is obtained with greater yields of refined product when this ratio is increased to 10:1, 30:1, or 50:1, or even higher. For example, when a propane to soybean oil ratio of approximately 30:1 is used, it is generally necessary to remove only about 1.5 percent of the crude soybean oil as bottoms in order to remove substantially all of the phosphatides, mucilaginous materials as well as some of the color bodies and polyfunctional fatty acids. These losses are far less than those encountered by the use of previously known processes. When relatively higher ratios of propane to soybean oil are used, the proportion of oil absorbed by the solvent is greater and the maximum temperature at the top of the tower 12 must be established with respect to the solvent to soybean oil ratio.

The temperature at the bottom of the tower must, of course, be above that temperature at which complete miscibility of the solvent and the soybean oil in the lower portion of the tower occurs. The preferred bottom temperatures are generally maintained at from about 5° to about 100° F. or more below the critical temperature of the solvent. When propane is employed as a solvent in the refinement of soybean oil, the temperature at the top of the tower may be between 150° and 200° F. and the bottom temperature may be between 140° and 190° F.

The pressure employed in the fractionating tower 12 is maintained sufficiently above the vapor pressure of the solvent to permit substantial variation in the tower pressure without reducing it below the vapor pressure of the solvent. A maximum operating pressure of approximately 50 pounds per square inch higher than the vapor pressure of the solvent is generally sufficiently high since adjustments of 10 to 15 pounds per square inch in the operating pressure are usually sufficient to counteract whatever temperature variations may occur in the operation of the tower. For example, the pressure in the tower 12 may be between about 400 and about 490 p. s. i. g., but is not restricted to this range.

When a portion or all of the partially refined soybean oil is introduced into fractionating tower 29, the temperatures required therein, in order to remove a small overhead fraction containing the sterols, tocopherols, free fatty acids, etc., are higher than those employed in the first fractionating tower 12 while still falling within the range of temperatures previously defined. For example, the temperature at the top of fractionating tower 29 may be between 165° and 210° F. while the temperature at the bottom of this tower may be between 160° and 195° F. Since the temperatures employed in fractionating tower 29 are slightly higher than in tower 12, it is also necessary to operate this tower at a slightly higher pressure. For example, the pressure in the tower 29 may be

between about 510 and 590 p. s. i. g., but is not restricted to this range.

As previously stated, when an efficient operation of tower 12 is employed, the material withdrawn through line 19 constitutes only about 1.5 percent of the crude soybean oil while the remaining 98.5 percent together with the propane is passed to fractionation tower 29. During efficient operation of this latter tower, all of the sterols, tocopherols, as well as some free fatty acids, may be completely removed from the soybean oil by withdrawing from 0.5 percent to 1.0 percent overhead based on the crude soybean oil. The material withdrawn from tower 29 through line 39, therefore, constitutes from 97.5 percent to 98 percent of the original oil and since a practically negligible quantity of material is removed in steam stripper 47, the final product will constitute from about 97 percent or higher of the crude oil. Though a negligible amount of material is removed in steam stripper 47, it has been found that this separation when used subsequently to the propane fractionation steps previously described, not only effectively removes odoriferous materials but also effects a remarkable decolorization of the soybean oil. For example, when a crude soybean oil has an initial color of 70Y-15R (Lovibond), it will be reduced in the first fractionating tower 12 to a color of approximately 30Y-3R (Lovibond), and when this material is finally treated in steam stripper 47, the color is further reduced to 10Y-2R (Lovibond), in spite of the fact that a total of less than 3 percent of the original crude oil has been removed. Not only is this decolorization step remarkable but it has also been found that the stability of the oil treated according to the present process, both as to odor and color, is greatly improved. In other words, it has been found that a highly decolorized soybean oil obtained by a treatment, according to the present invention, will retain its exceptional color property for a much longer period of time than was previously the case.

In order to effectively strip the soybean oil in stripper 47, it is generally best to maintain the stripper at a pressure about between 1 mm. and 20 mm. but preferably within the range of from about 8 mm. to 12 mm. The temperature of this operation and of the steam being introduced into the stripper is usually between about 350° F. and 500° F., but a temperature of about 425° F. has been found to be most suitable.

Example I

Tests of a typical neutralization of soybean oil by the present method reveal the following fatty acid contents:

	Percent fatty acids
Crude oil	0.5
98% overhead phase material	0.46
2% bottoms material	2.5
98% overhead after steam treatment	0.02

The above example reveals that only 10 percent of the original fatty acids were removed by the propane fractionation. This is not to be considered insignificant, however. This 10 percent comprises 0.05 percent of the original oil, which would be more than could be tolerated in satisfactorily neutralized oil. Moreover, the example above is taken from the treatment of first grade fresh soybean oil. In the case of inferior oils, 20 to 30 percent of the fatty acids were removed in the bottoms fraction of the propane fractionation.

The stability as to odor and flavor is also improved by the foregoing treatment. However, soybean and other vegetable oils tend to acquire objectionable odors and tastes under certain conditions of usage or storage.

Example II

Soybean oil was decolorized in a 4-inch baffled tower as a stripping tower and a 2-inch tower packed with 3/8-inch Lessing rings as the rectifying tower. A propane

stream was divided with equal portions, 8.40 percent by weight, being introduced at the 16-foot point of the stripping tower and at the 16-foot point of the rectifying tower. With a tower top temperature of 165° F. and a bottom temperature of 158° F., an overhead product amounting to 97.6 percent was made using a reflux ratio of 0.65, based on the overhead.

The decolorized overhead product was then refracted using a pair of 18-foot towers two inches in diameter, with a propane to oil ratio of 29.8 by volume. The oil feed rate was 3,000 cc. per hour and the tower temperatures were 193° F. top and 176° F. bottom. Using a reflux ratio of 56.4 based on overhead, the yield of the overhead product amounted to 1.6 weight percent. The data are as follows:

TABLE I

Propane fractionation in countercurrent towers—Tabulation of data—Soybean oil

Percentage of Original Oil	100	196.2
Type of Operation	Temperature Gradient + Reflux	
No. of Towers	2	2
Yields and Balances (Output Basis):		
Oil—Weight Percent—		
Overhead	97.6	1.6
Bottoms	2.4	98.4
Weight Balance	102.1	102.6
Free Fatty Acid Recovery, Percent—		
Overhead	94.7	81.4
Bottoms	1.9	15.9
Total	96.6	97.3
Unsaponifiable Oil Recovery, Percent—		
Overhead	99.0	48.8
Bottoms	3.9	45.6
Total	102.9	94.4
Operating Conditions:		
Temperature, ° F.—		
Top	165	193
Feed	158	182
Bottom	158	176
Temperature Gradient, ° F./Ft.—		
Rectifying Section	0.28	0.55
Stripping Section	0.00	0.50
Throughput, Lb./Hr./Sq. Ft.—		
Fractionating Tower (2-in. Tower):		
Oil	261.5	261.5
Propane	4,290	4,290
Propane Velocity, ft./hr.—		
Fractionating Tower (2-in. Tower)	136.5	136.5
Propane-Oil Ratio (By Volume, 60°)—		
Fractionating Tower	30.0	29.8
Propane-Oil Ratio, By Weight—		
Fractionating Tower	16.4	16.4
Contact Time, Min.—		
Fractionating Tower	36.8	15.3
Reflux Ratio	0.65	56.4
Height of Rectifying Section, Ft.	25	20
Height of Stripping Section, Ft.	7	12
Oil Properties:		
Feed		
Color, Lovibond:		
Red		
Yellow		
Color, Gardner	11+	10—
Free Fatty Acids, Percent (As Oleic)	0.68	0.68
Unsaponifiable Oil, Wt. Percent	0.70	0.95
Saponification No.	191	191
Iodine No. (Wijs)	136	135
Moisture and Volatility, Wt. Percent	0.2	
Acetone Insoluble, Wt. Percent	0.3	
Gardner Break	0.05	
Specific Gravity (60°/60°)	0.921	0.919
Fractionator Overhead—		
Color, Lovibond:		
Red		
Yellow		
Color, Gardner	9	8—
Free Fatty Acids, Percent (As Oleic)	0.66	34.6
Unsaponifiable Oil, Wt. Percent	0.71	29.0
Saponification No.	192	138
Iodine No. (Wijs)	135	127
Moisture and Volatility, Wt. Percent		
Acetone Insoluble, Wt. Percent		
Specific Gravity (60°/60°)	0.919	0.917
Bottoms—		
Color, Gardner	15+	10—
Free Fatty Acids, Percent (As Oleic)	0.54	0.11
Unsaponifiable Oil, Wt. Percent	1.15	0.44
Iodine No. (Wijs)	141	134
Saponification No.	196	192
Acetone Insoluble, Wt. Percent	1.9	
Moisture and Volatility, Wt. Percent		
Specific Gravity (60°/60°)	0.934	0.919

TABLE I—Continued

Observed Yields:		
Oil, Weight Percent—		
Fractionator Overhead Sample.....	99.7	1.6
Bottoms.....	2.4	101.0
Total.....	102.1	102.6
Free Fatty Acid Recovery, Percent—		
Overhead.....	96.8	81.4
Bottoms.....	1.9	16.3
Total.....	98.7	97.7
Unsataponifiable Oil Recovery, Percent—		
Overhead.....	101.1	48.8
Bottoms.....	3.9	46.8
Total.....	105.0	95.6
Detailed Operating Conditions:		
Flow, Gm./Hr.—		
Feed.....	2,772	2,773
Propane to Fractionator.....	² 45,500	45,500
Fractionator Overhead Sample.....	2,763	43
Bottoms.....	66	2,802
Reflux (Oil).....	1,790	2,430
Intermediate Overhead.....	3,510	1,520
Intermediate Bottoms.....	799	1,470
Propane-Oil Ratio (Stream Samples)—		
Overhead Receiver.....	0.30	0.30
Intermediate Bottoms.....	2.40	2.0
Pressure, lb./sq. in. Ga.—		
Fractionating Tower.....	490	670
Overhead Receiver.....	350	460
Temperature, ° F.—		
E-2 Tower:		
Top.....	165	193
2.....	164	192
3.....	164	190
4.....	164	188
5.....	164	186
6.....	163	184
E-1 Tower:		
Top.....	159	184
2.....	159	182
3.....	159	180
4.....	158	179
5.....	158	178
6.....	158	176
E-8 Tower:		
Top.....		
Bottom.....		
Oil Inlet.....	157	181
Propane Inlet.....	158	176
Overhead Receiver.....	210	210
Transfer Line.....	164	183
Position of Entering Streams (Distance from Top of Tower, Ft.)—		
Stripping Tower (18' Twr., 4" Dia.) (E-1):		
Feed.....	9	4
Propane.....	² 16	16
Raffinate Rectifying Tower.....	1	1
Rectifying Tower (18' Twr., 2" Dia.) (E-2):		
Reflux.....	4	4
Extract Stripping Tower.....	16	16
Propane.....	² 16	

¹ Overhead product—contains some unofficial material.² Propane stream divided—Equal amount to each tower.

Freshly refined soybean oil made from a crude oil derived from high grade beans has a characteristic odor but is bland and sweet. It can be considered to be high-class salad oil since the characteristic odor is not objectionable. However, when heated to 425° F. in a so-called "cooking test," a sharp, "grassy" odor develops. The chief drawback of refined soybean oil is that in the course of from a few days to months, depending upon conditions, the oil undergoes a peculiar change which is known as "reversion." This deterioration is accompanied by the development of an undesirable odor and flavor which has been variously described as "cucumbery," "grassy," "painty," or "fishy." There is undoubtedly a progressive change in odor and flavor, and the odor is not the same at the beginning of the reversion period as toward the end. The process is not true odor reversion because the odor does not revert to that of either the crude oil or the undeodorized oil.

It should be observed that reversion and oxidative rancidity are different, although possibly related, phenomena. Corn oil, one of the best food oils, causes little trouble because of reversion but becomes rancid more rapidly than soybean oil as measured by peroxide formation. Attempts to correlate soybean oil reversion with peroxide values have not led to fruitful results.

A tremendous amount of research effort has been ex-

pended in attempting to prevent soybean oil reversion and to determine the underlying cause. The theory that has attracted the largest following in recent years is that soybean oil reversion is due to the presence of a small percentage of linolenic acid, an unsaturated fatty acid containing three double bonds, in the glyceride molecules. Corn and cottonseed oil, which are not subject to much reversion, do not contain a detectable amount of linolenic acid. On the other hand, linseed oil which contains a high percentage of linolenic acid is characterized by a typical strong "painty" odor. According to this theory, the linolenic acid decomposes in storage to odoriferous substances because of oxidation with air, condensation, ring closure, or some unknown kind of reaction.

On this assumption work on the reversion problem has been directed toward the elimination of linolenic acid. Since it is impractical in this case to remove the linolenic acid by hydrolysis of the glycerides and separation of the fatty acids, the main line of attack has been partially and selectively to hydrogenate the oil with the objective of converting the linolenic acid to a more saturated acid such as linoleic. Unfortunately, the partial hydrogenation has not been amenable to selectively control with the result that stearines and solid isomeric unsaturated acids are formed to an undesirable extent. Furthermore, reversion is not entirely prevented and the oil acquires in addition a "gassy" odor.

The invention herein disclosed makes it possible to remove the free fatty acids, including substantially all of the free linolenic acid, without neutralization treatment of the oil. Decolorizing is accomplished without the use of any bleaching agent or adsorbent means in the body of the oil. All or a part of the condensate recovered from condenser 50 through line 51 may be subjected to neutralizing treatment (preferably with aqueous alkali solution) and to decolorizing by means of carbon or clay filter beds or to bleaching by heat, steam, or chemical treatment. The neutralized or decolorized condensate may then be washed with water to remove soaps and residual alkali and returned to the refined oil.

The refined soybean oil, according to the present invention, will meet the severest standards required in both the paint and varnish industry as well as the food industry. This refined material may be obtained far more efficiently and by a method which is far simpler than those methods previously used. In addition, the product so obtained has less odor and color reversion and far smaller losses are incurred during the processing of the oil.

The present invention has been described with particular reference to a specific embodiment thereof, but it will be recognized that I do not intend to be limited by this description, but rather that the scope of the present invention should be defined solely by the appended claims.

I claim:

1. A method for refining vegetable oil which includes the steps of: contacting said oil with a solvent having a critical temperature of less than 450° F. under paracritical conditions to fractionate said oil into an extract phase containing substantially all of said oil and a raffinate phase containing color bodies and substantially all the polyfunctional acid content of said oil; withdrawing said extract phase and subjecting the extract oil contained therein to treatment with steam at a temperature between 300° F. and 500° F. to vaporize volatile materials; condensing said vaporized materials and neutralizing them with an alkali; and recombining at least part of said neutralized condensate with said extract oil.

2. An improved process for producing a refined neutral soybean oil by fractionation with a solvent having a critical temperature of less than 450° F. under paracritical conditions, which process includes the steps of: contacting said oil with said solvent in a first vertically extended countercurrent fractionation zone at temperatures adjusted within the paracritical range to form two counterflowing phases, an extract phase containing substan-

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tially all of the oil, and a raffinate phase containing substantially all of the polyfunctional fatty acid content of said oil; contacting at least part of said extract phase with said solvent in a second fractionation zone to form a secondary extract phase containing substantially all the unsaponifiable content and a secondary raffinate phase containing most of the oil; withdrawing said secondary extract and raffinate phases from the upper and lower ends respectively of said second fractionation zone; subjecting the oil content of said secondary raffinate phase to treatment with steam at a temperature between 350° F. and 500° F. to remove vaporizable impurities and substantially all remaining unsubstituted fatty acids; and combining at least part of the unsaponifiable concentrate in said secondary extract with said secondary raffinate after said steam treatment.

3. A method for refining vegetable oil which includes the steps of: contacting said oil with a solvent having a critical temperature of less than 450° F. under paracritical conditions to fractionate said oil into an extract phase containing substantially all of said oil and a raf-

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finat phase containing color bodies and substantially all the polyfunctional acid content of said oil; withdrawing said extract phase and subjecting the extract oil contained therein to treatment with steam at a temperature between 300° F. and 500° F. to vaporize volatile materials; condensing, neutralizing with an alkali; and recombining at least part of said vaporized material with said extract oil.

4. A process as described in claim 3 in which prior to the recombination of said condensate with said oil, said condensate is decolorized.

References Cited in the file of this patent

UNITED STATES PATENTS

2,118,454	Schaafsma	May 24, 1938
2,394,968	Van Orden	Feb. 12, 1946
2,432,021	Larner	Dec. 2, 1947
2,454,638	Dickinson et al.	Nov. 23, 1948
2,508,387	Hixson et al.	May 23, 1950
2,521,234	Leaders et al.	Sept. 5, 1950