

Sept. 21, 1943.

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2,329,889

PROCESS FOR REFINING FATTY MATERIAL

Filed Jan. 11, 1941

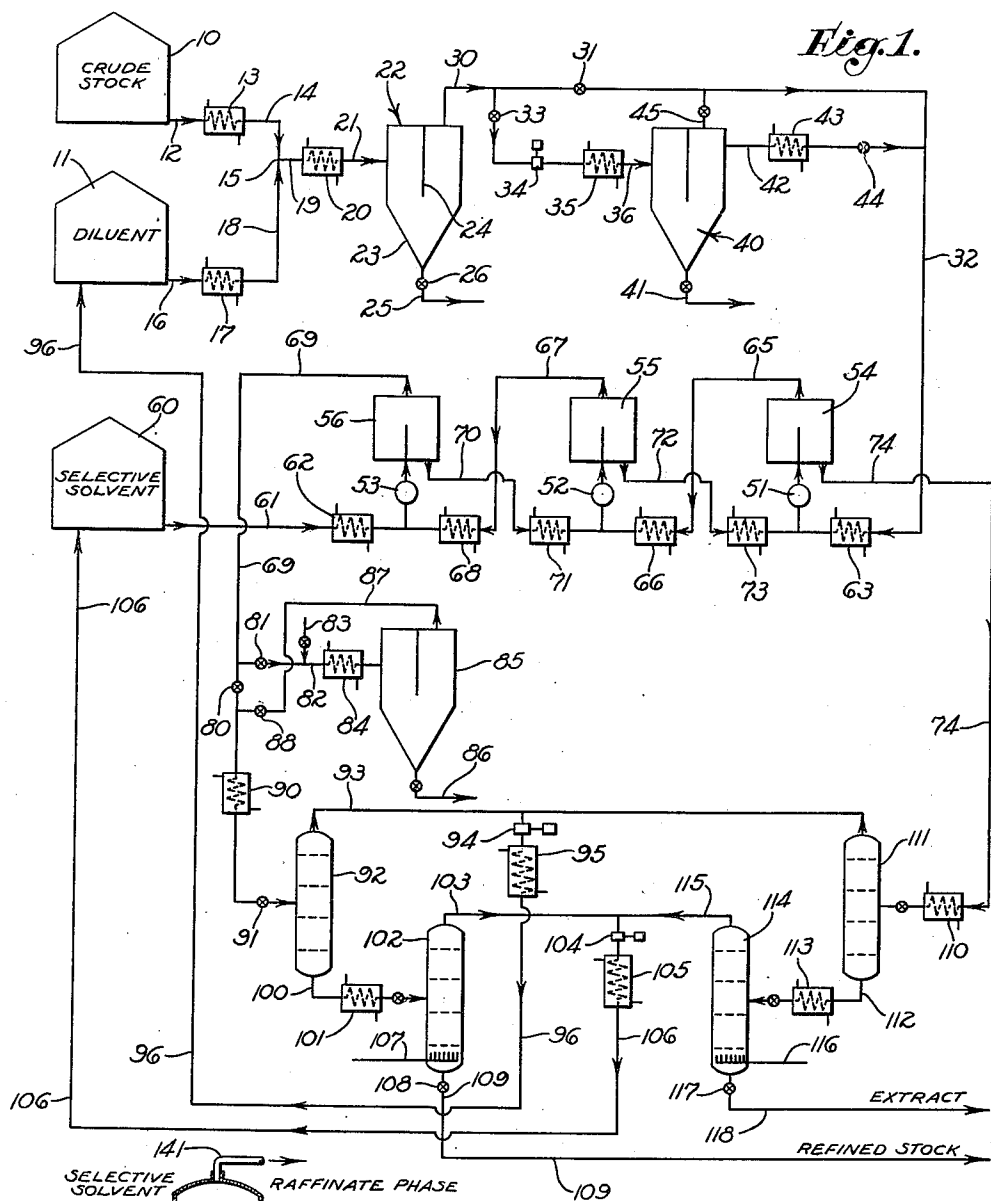


Fig. 1.

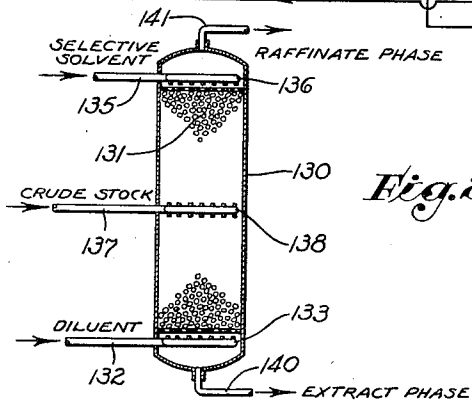


Fig. 2.

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UNITED STATES PATENT OFFICE

2,329,889

PROCESS FOR REFINING FATTY MATERIAL

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Application January 11, 1941, Serial No. 374,132

10 Claims. (CL 260—428.5)

This invention relates to the treatment and refining of fatty materials and glyceride oils, and relates more particularly to a method of solvent refining such materials.

Fats and oils are conventionally refined by treatment with chemical reagents. Objections to such treatment include the refining loss of good oil, the consumption of reagents, and the degradation of the materials acted upon. For example, in the alkali refining of glyceride oils, there is both a saponification and entrainment loss of good oil, a conversion of the fatty acids in the soapstock foats, and a substantial consumption of reagents, including both the original alkali and the acid subsequently employed to acidulate the soapstock.

It is possible to overcome these objections by recourse to solvent refining, i. e., to extract the fatty material with solvent which is selective and which preferentially extracts the undesired constituents, or which forms with the fatty material a system of conjugate phases, one of which, the extract phase, is relatively rich in undesired constituents and the other of which, the raffinate phase, is relatively rich in the desired constituents.

The solubility characteristics of the various normal constituents of fats do not differ greatly apart from certain minor constituents, such as gums and resins, and it is, accordingly, difficult to find a solvent which will exercise the desired preferential and selective action.

It is an object of the present invention to provide a method for the solvent refining of fatty materials which overcomes the stated difficulties and which greatly increases the spread between desired and undesired constituents with regard to their distribution in the extract and raffinate phases.

The present invention is based, in part at least, on the discovery that, in the presence of suitable diluents, the degree of differential extraction of glyceride oils with a given extractive solvent may be greatly increased, particularly if the diluent employed is selected from the class of liquefied, normally gaseous hydrocarbons, typically and preferably liquefied propane.

It is an object of the present invention to provide a method for treating fatty materials with a plurality of solvents, one being primarily a diluent and the other a selective solvent adapted to extract certain selected constituents.

Further objects and aspects of the invention will become apparent in the following discussion,

made with special reference to the drawing, in which:

Figure 1 is a flow diagram with schematic representations of apparatus suitable for carrying out my process; and

Figure 2 is a cross section of an extraction tower suitable for carrying out a modified form of my process.

Referring more particularly to Figure 1, 10 is a tank containing the crude stock, such as unrefined fatty oil, and 11 is a tank containing the diluent, preferably a pressure tank adapted to hold liquefied propane. The crude stock is withdrawn through a line 12 and brought to a suitable temperature in a heat exchanger 13, whence it is conducted by a pipe 14 to a junction point 15. The diluent is withdrawn by means of a pipe 16, brought to a suitable temperature in a heat exchanger 17, and thence conducted by means of a pipe 18 to the aforesaid juncture 15. The commingled streams formed at the juncture 15 are passed by means of a pipe 19 to a heat exchanger 20 in which the temperature of the combined streams may be further modified, and the resulting solution or admixture is then passed by means of a pipe 21 to a separator, illustrated as a decanter 22. The decanter comprises a closed shell 23 having an interior partly divided by a baffle 24 and having a lower draw-off line 25 through which, by means of opening a valve 26, material separating and settling from the propane-oil solution may be withdrawn. Such materials are normally comprised of gums, phosphatides, resins, and the like, which are commonly termed "minor impurities."

The clarified propane-oil solution is withdrawn from the upper part of the decanter 22 by means of a draw-off line 30 and may, if desired, be sent directly to subsequent solvent extraction equipment by opening a valve 31 leading into a header 32. In most instances, however, it is possible to precipitate a substantial quantity of additional impurities from the propane-oil solution by further altering its physical state, as by cooling or heating. For this purpose, the valve 31 may be closed and a valve 33 opened leading into the suction of a pump 34, which may be operated to maintain the desired pressure conditions during subsequent heating.

The discharge from the pump 34 is passed through a heat interchanger 35, where it is brought to the desired temperature, and it is then passed by means of a pipe 36 into a second separator, illustrated as a decanter 40. Additional impurities separating from the propane-

oil solution at this point may be withdrawn by means of a valved withdrawal line 41 at the bottom of the decanter, and the clarified (and at least partially purified) propane-oil solution removed through a draw-off line 42 through a heat exchanger 43, which may serve as a cooler in case high temperature precipitation is employed in the second decanter, and thence through a back-pressure valve 44 which is adjusted to maintain the desired pressure on the decanter 40. Diluent vapors may also be withdrawn from the decanter 40, if desired, by means of a vapor withdrawal line 45.

The clarified propane-oil solution from either the first or second decanter is gathered in the header 32 and thence passed to a solvent extraction plant. The solvent extraction plant typified in the drawing is a three-stage countercurrent plant comprising mixers 51, 52, and 53 and settling vessels 54, 55, and 56. A selective solvent contained in a tank 60 is withdrawn by means of a pipe 61, passed through a heat exchanger 62, and thence passed into a mixer 53. The propane-oil solution in the header 32 is passed through the heat exchanger 63 and thence into the mixer 51.

Each mixer receives a commingled stream of propane-oil or raffinate phase largely constituted by the propane-oil, and a selective solvent or an extract phase largely constituted by a selective solvent. These streams are thoroughly admixed in the mixer to form a set of conjugate phases which are in substantial equilibrium, and this mixture then passes to the settling vessel where it layers out into an upper raffinate phase and a lower extract phase.

Accordingly, the path of the oil-diluent, or the raffinate phase resulting therefrom, is from the heat exchanger 63 to the mixer 51, thence to the settling vessel 54 to form a raffinate phase which is withdrawn by means of a pipe 65 leading to a heat exchanger 66, thence to the mixer 52 and into the settling vessel 55 to form a raffinate phase which is withdrawn by means of a pipe 67 conducting same to a heat exchanger 68, thence to the mixer 53, and thence to the settling vessel 56 to form a raffinate phase which is withdrawn by means of a pipe 69.

The path of the selective solvent, or the extract phase rich in the selective solvent, is virtually countercurrent to the above and is from the heat exchanger 62 to the mixer 53, to the settling vessel 56 to form an extract phase which is withdrawn by means of a pipe 70 and conducted to a heat exchanger 71, thence to the mixer 52 and settling vessel 55 to form an extract phase which is withdrawn by means of a pipe 72 and conducted to a heat exchanger 73, and thence to the mixer 51 and settling vessel 54 to form a final extract phase which is withdrawn through a pipe 74.

The raffinate phase withdrawn through the pipe 69 comprises the desired constituents of the crude stock and most of the diluent employed, and may, under certain circumstances, contain some small amount of selective solvent. In case it is desirable to exercise some further chemical refining of the oil, this chemical refining is best practiced on the diluted raffinate phase as obtained at this point. Thus, for example, the raffinate phase may be chemically or physically treated by direct admixture with a refining reagent (such as a solution of caustic alkali or soda ash) or with a slurry of clay, or the like.

For this purpose, a valve 80 in the pipe 69

is closed and a valve 81 is opened leading to a pipe 82. A valved inlet pipe 83 permits the introduction of clay slurry, caustic alkali, or other reagent into the stream flowing through the pipe 82. The resulting admixture may be passed through a heat exchanger 84 to bring it to optimum refining temperature, and thence to a decanting or other separating vessel 85 having a lower draw-off line 86 through which soapstock, spent clay, or the like may be withdrawn. The purified raffinate phase is withdrawn from the top of the decanter 85 through a pipe 87 and this material may then be returned to the pipe 69 by means of a valve 88. If desired, the chemical refining equipment may be by-passed by closing the valves 81 and 88 and opening the valve 80.

The raffinate, with or without additional chemical refining, is subjected to a step of distillation to recover the diluent and such of the selective solvent as may be dissolved in or mechanically admixed with the raffinate phase, whereby a refined oil free from diluent or associated solvents is ultimately obtained.

A suitable distillation method is shown in the drawing and comprises passing the raffinate phase from the pipe 69 through a heater 90 where it is brought to a temperature sufficient for the flash distillation of the diluents, such as propane, and thence through a valve 91 into a flash rectifying column 92, wherein the propane vapors are sent overhead through a vapor line 93 to the intake of a compressor 94.

The compressed vapors or liquids issuing from the compressor 94 are cooled or condensed in a condenser 95 to form a liquefied diluent which is returned to the diluent tank 11 by means of a return line 96.

The residual fraction or bottoms from the rectifying tower 92 are withdrawn by means of a line 100. This material is virtually free of diluents at this stage but may still contain some selective solvent due to mechanical entrainment or partial miscibility in the solvent refining stage. The bottoms are accordingly further heated in a heat exchanger 101 and sent to a stripping tower 102 wherein all trances of solvent or other low boiling materials are removed as a vaporous overhead. The overhead vapors are withdrawn through a vapor line 103 and passed to the suction of a pump 104, which is preferably arranged to maintain subatmospheric pressure on the stripping column 102. The discharge of the pump 104 is passed through a condenser 105 and the condensed solvent is returned by means of a pipe 106 to the selective solvent tank 60.

If desired, the stripping action in the column 102 may be aided by the injection of steam through a steam pipe 107. The bottom fraction from the tower 102 is withdrawn through a valve 108 into a discharge line 109. These bottoms constitute the refined stock and, as such, are the principal product of my process.

The extract phase withdrawn through the line 74 consists preponderantly of selective solvent and the undesired constituents of the crude stock. There may be present in this phase some quantity of diluent due to effects of mechanical entrainment or partial miscibility. This extract phase is subjected to distillation steps similar in principle to those described in connection with the raffinate phase and illustrated, for purposes of simplicity, as being conducted in the same type of apparatus. It will be understood, however, that, with the raffinate phase, the chief

overhead product is diluent, whereas, with the extract phase, the chief overhead product is solvent, and that, in practice, these distinctions will make for the use of different sized towers, different levels of temperature, and the like, in handling the two phases. Schematically, however, the extract phase is passed through a heat exchanger 110 and into a flash tower 111 where any diluent is vaporized and sent overhead to the suction of the compressor 94. The bottoms of the tower 111 are passed by means of a pipe 112 to a heat exchanger 113, and thence into a solvent recovery tower 114 in which the solvent is taken overhead through a line 115 to the suction of the pump 104. The bottoms from the tower 114, which may be subjected to stripping with steam, if desired, by injecting steam through a pipe 116, are withdrawn from the tower 114 by means of a valve 117 leading into a pipe 118.

These bottoms in the pipe 118 are completely free from diluent and selective solvent and comprise the fractions which it was desired to remove from the refined stock. It will be noted that this extract material is obtained substantially unmodified by any chemical action, which is very advantageous in many instances.

In some instances, it is preferable to subject the stock to the simultaneous action of counter-current streams of diluent and selective solvent. An extraction tower adapted to carry out this type of treatment is shown in Figure 2 and comprises an extraction tower 130 partially filled with inert contact masses 131. The diluent, having a low specific gravity, is introduced near the bottom of the tower through a line 132, the injected diluent being preferably distributed by use of an upwardly directed spray ring 133.

The selective solvent, having a relatively high density, is introduced into the column 130 near the top thereof by means of a pipe 135 in communication with a downwardly directed spray ring 136. The crude stock is injected near the middle of the column by means of a pipe 137 terminating in a spray head 138.

The selective solvent descends through the column, extracting the undesired constituents and forming an extract phase which is removable from the bottom of the column by means of an extract draw-off line 140. The diluent rises through the column and dissolves the desired fractions of the oil to form a raffinate phase which is withdrawable from the upper end of the column through a draw-off line 141. These phases may be distilled or otherwise handled, as exemplified in the discussion of Figure 1.

As the diluent, I prefer to employ low molecular weight water-immiscible material, such as liquefied normally gaseous hydrocarbon, including ethane, propane, and butane. Liquefied propane or commercially available mixtures which are largely propane but which may contain some ethane, butane, and the like, constitute a particularly advantageous diluent.

The relative proportions of diluents and crude stock may be varied over a wide range. For example, with one volume of crude stock, a fraction of a volume up to eight or ten volumes of diluent may be employed.

The liquefied normally gaseous hydrocarbons, and, in particular, propane, exercise a precipitating action on minor impurities such as gums, resins, phosphatides, and the like. Provision is made for the preliminary segregation of such materials in Figure 1 in the decanters 22 and 40. When operating in accordance with Figure 2, the

minor impurities are, for the most part, dissolved in the extract phase.

Temperature is frequently an important factor in the precipitation of the minor impurities. When using several volumes of propane for the volume of crude stock, minor impurities may be substantially precipitated at room temperature, and, by chilling, further quantities may be precipitated. If desired, this additional precipitation by further chilling may constitute a second stage, for example, as effected in the decanter 40. However, it is frequently advisable to carry out a second stage of precipitation at substantially elevated temperatures, for example, 150° F or higher. At these temperatures, the liquid propane undergoes a substantial reduction in solvent power due to the fact that it is approaching its critical temperature, and additional quantities of impurities or undesired fractions may accordingly be precipitated by conducting the second stage at substantially elevated temperature.

The choice of a selective solvent depends, in large part, on the character of the crude stock and the constituents which it is desired to remove. As a typical instance, in treating certain crude glyceride oils, the undesired constituents will normally be regarded as consisting largely of free fatty acids. Various solvents may be used to extract the free fatty acids of the propane-oil solution, such solvents including, but not being limited to, alcohols, ketones, aldehydes, low molecular weight organic acids, etc. These solvents may be anhydrous, e. g., glacial acetic acid or anhydrous ethyl alcohol, but in many instances they may be advantageously associated with sufficient water to reduce or prevent their miscibility with the liquefied normally gaseous hydrocarbon diluent. Isopropyl alcohol containing from 5% to 20% of water is a good selective solvent for fatty acids.

Various other selective solvents may also be employed in the present process, these solvents in general being characterized by their relatively polar character, high internal pressure, and relatively restricted miscibility with liquefied propane or other liquefied normally gaseous hydrocarbon. In this connection, there may be mentioned phenol, cresylic acids, nitrobenzene, sulphur dioxide, dichlorethyl ether, and the like.

The character and quantity of selective solvent will be varied according to the material worked upon and the separation which is desired. Thus, for example, in solvent refining a crude glyceride oil to remove a few per cent of free fatty acids, a relatively small amount of selective solvent having a relatively low solvent power, for example, aqueous isopropyl alcohol, may be employed. If it is desired to solvent fractionate the glyceride constituents themselves according to molecular weight, unsaturation, and general chemical character of the fatty acids combined with the glycerine, then substantially larger quantities of a more powerful solvent, such as sulphur dioxide, phenol, or the like, may be employed. Or, again, the crude stock may consist largely of a complex mixture of free fatty acids which it is desired to segregate on the basis of their solubility characteristics, in which case solvents such as phenols, alcohols, etc., may be advantageously employed.

Modifying agents may be employed to modify the solvent power of the selective solvent. Thus, the selective solvent, which, in the majority of instances, will be partially miscible with water, may be associated with more or less water to

modify its solvent power. In some instances, an alkaline agent, preferably a volatile alkali, such as ammonia, may be incorporated in the selective solvent, particularly where the extraction of acidic constituents is desired. The volatile alkali may be largely recovered in distillation of the extract since the dissociation temperatures of ammonia soaps are relatively low.

In some instances, the solvent may be modified subsequent to phase separation, as by the addition of water to an extract phase formed by the action of a water-soluble selective solvent to precipitate the fatty acids or other extracted oleaginous constituent.

The temperature of solvent extraction should, in general, be sufficiently below the critical solution temperature for the system concerned to insure the formation of conjugate phases. Depending upon the character of the stock, the selective solvent employed, and various other factors, subatmospheric, atmospheric, or superatmospheric temperatures may be indicated as optimum for the process of solvent extraction. In many instances, it is desirable to maintain a temperature gradient throughout the countercurrent extraction such that the highest temperature is maintained in the zone from which the final raffinate is taken. A plurality of intermediate heat exchangers are shown in Figure 1 for the purpose of establishing any desired temperature gradient in the extraction zone.

In the present specification and claims, the term "fatty materials" is to be understood as generic to glyceride oils, fats, fatty acids, and like educts or products of animal or vegetable fats and oils.

It will be understood that the details of the above examples are not limiting, and that various modifications of the described process may be practiced without departing from the scope of the appended claims.

I claim as my invention:

1. The process of refining glyceride oils containing free fatty acids to separate free fatty acids from said oil, which comprises, commingling the oil with a liquefied normally gaseous hydrocarbon and a selective solvent for said fatty acids which is substantially immiscible with said oil in the presence of said liquefied hydrocarbon, maintaining the materials under sufficient pressure to retain said hydrocarbon in liquid form so as to produce a liquid extract phase containing said selective solvent and free fatty acids and a raffinate phase containing substantially all of the glycerides of said oils and separating said phases by difference in specific gravity.

2. The process defined in claim 1 in which the selective solvent is iso-propyl alcohol.

3. The process defined in claim 1 in which the selective solvent is miscible with water and is employed in admixture with water.

4. The process defined in claim 1 in which the selective solvent comprises iso-propyl alcohol in admixture with water.

5. The process defined in claim 1 in which the selective solvent contains an alkaline reagent.

6. The process of refining crude glyceride oils containing gummy materials and free fatty acids, which comprises the steps of, mixing said glyceride oil with a liquefied normally gaseous hydrocarbon to dissolve the fatty material of said oils and precipitate gummy material, separating the precipitated gummy material from said fatty material, thereafter treating the fatty material with a selective solvent for fatty acids which is substantially immiscible with said oil in the presence of said liquefied hydrocarbon, maintaining the materials in said process under sufficient pressure to retain said hydrocarbon in liquid form so as to produce a liquid extract phase containing said selective solvent and free fatty acids and a raffinate phase containing substantially all of the glycerides of said oils and separating said phases by difference in specific gravity.

7. The process defined in claim 6 in which the liquefied normally gaseous hydrocarbon is propane and the selective solvent is iso-propyl alcohol in admixture with water.

8. The process defined in claim 6 in which said raffinate phase containing said liquefied hydrocarbon is further treated with a neutralizing agent to neutralize residual free fatty acids and form soap stock and in which said soap stock is separated from said phase.

9. The process defined in claim 6 in which said raffinate phase containing said liquefied hydrocarbon is further treated with a decolorizing agent and the decolorizing agent separated from said phase.

10. The process of refining glyceride oils containing free fatty acids to separate free acids from said oil, which comprises, continuously introducing a stream of said oil into a body of oil at an intermediate level in an extraction zone containing said body of oil, continuously introducing a stream of a liquefied normally gaseous hydrocarbon into said body of oil at a lower level in said zone below said intermediate level, whereby said hydrocarbon is commingled with said oil and moves upwardly therethrough, continuously introducing a stream of a selective solvent of fatty acids which is substantially immiscible with said oil in the presence of said hydrocarbon into said body of oil at an upper level in said zone above said intermediate level, said selective solvent having a greater specific gravity than said oil, whereby said solvent commingles with said oil and moves downwardly therethrough in the presence of said hydrocarbon, continuously withdrawing a raffinate phase containing said hydrocarbon and substantially all of the glycerides of said oil from said zone at a level above said upper level and continuously withdrawing a solvent phase containing solvent and free fatty acids from said zone at a level below said lower level.

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