Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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Fig. 2.

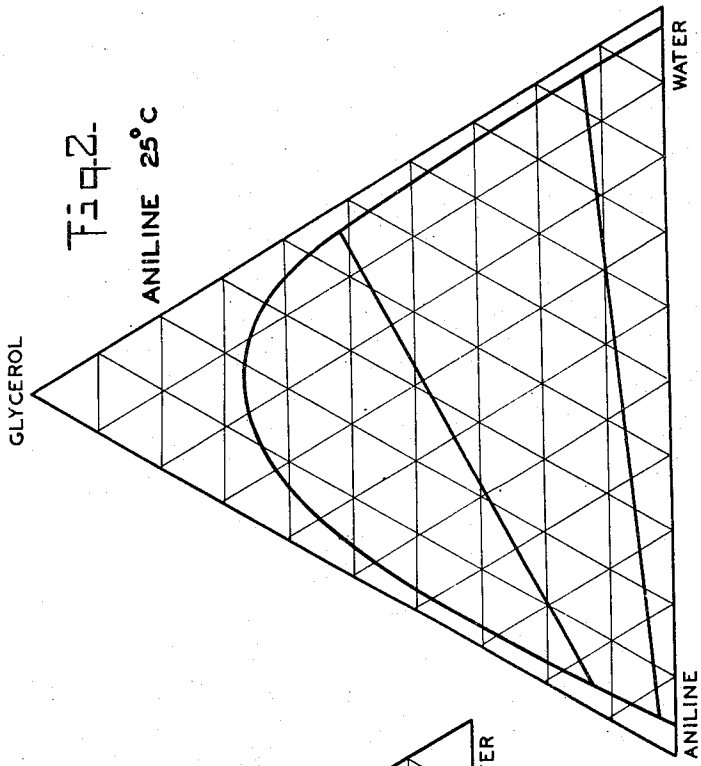
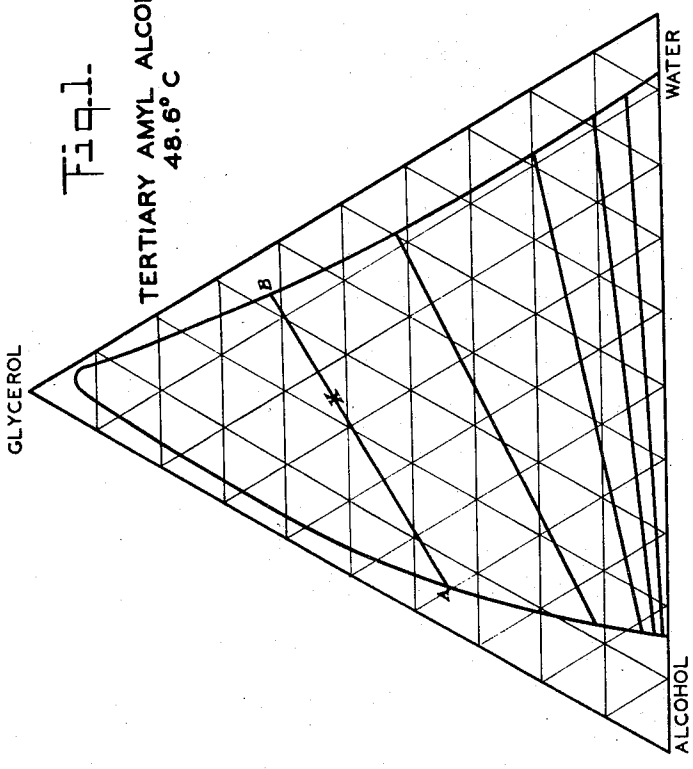


Fig. 1.



INVENTOR.
JOSEPH CLIFTON ELGIN

BY Trenton Meredith
ATTORNEY

Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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Fig. 4.

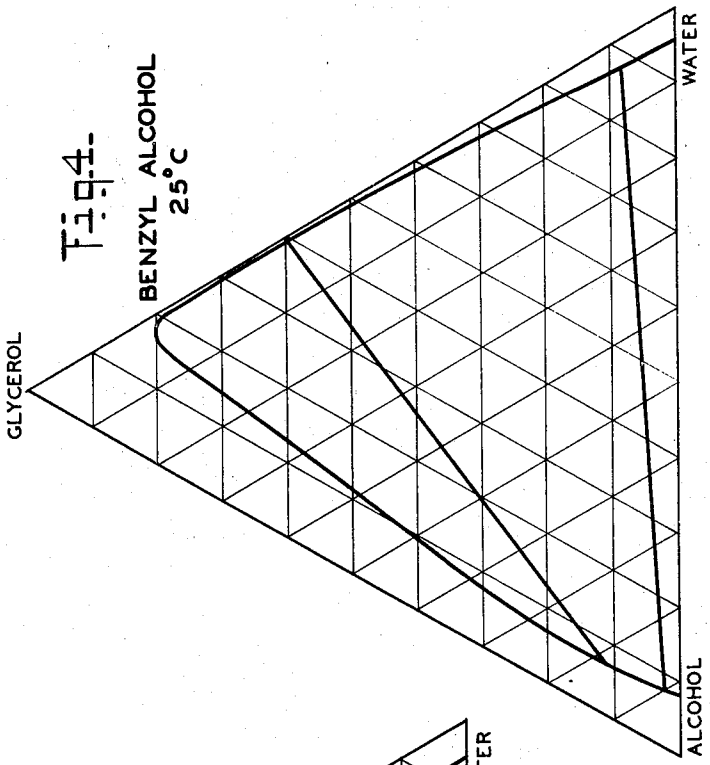
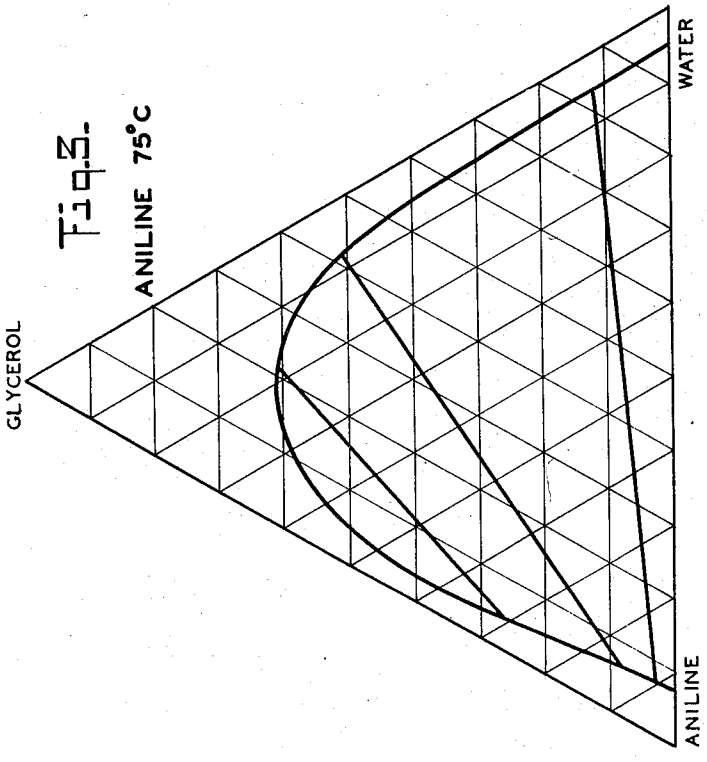


Fig. 5.



INVENTOR.
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BY Trenton Meredith
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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Fig. 6.

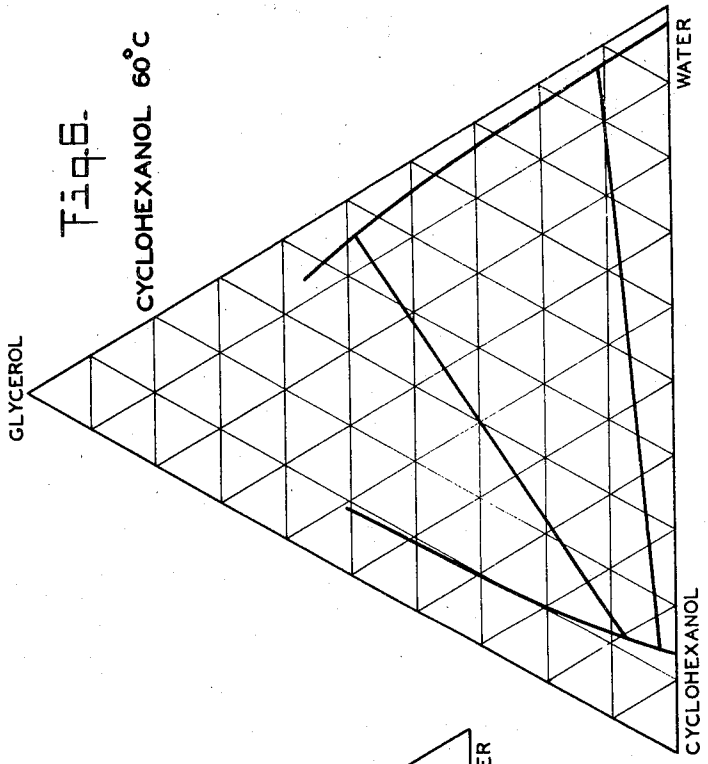
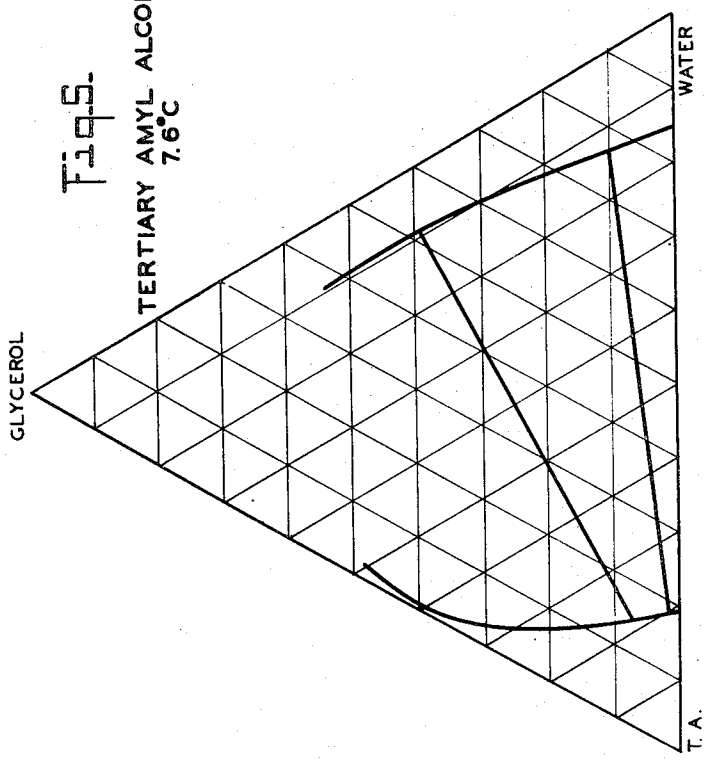


Fig. 5.



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GLYCERINE EXTRACTION PROCESS

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Fig. 8.

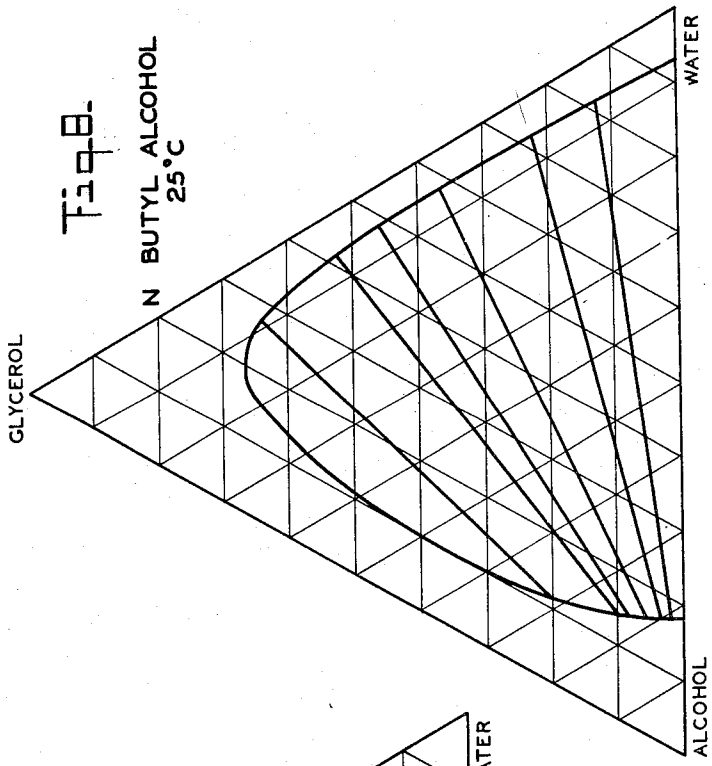
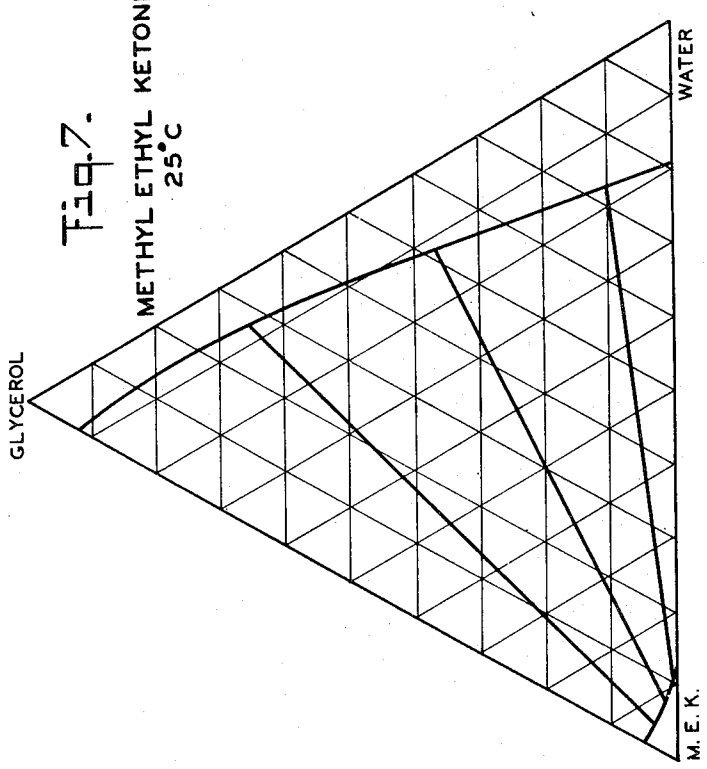


Fig. 7.



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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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Fig. 10.

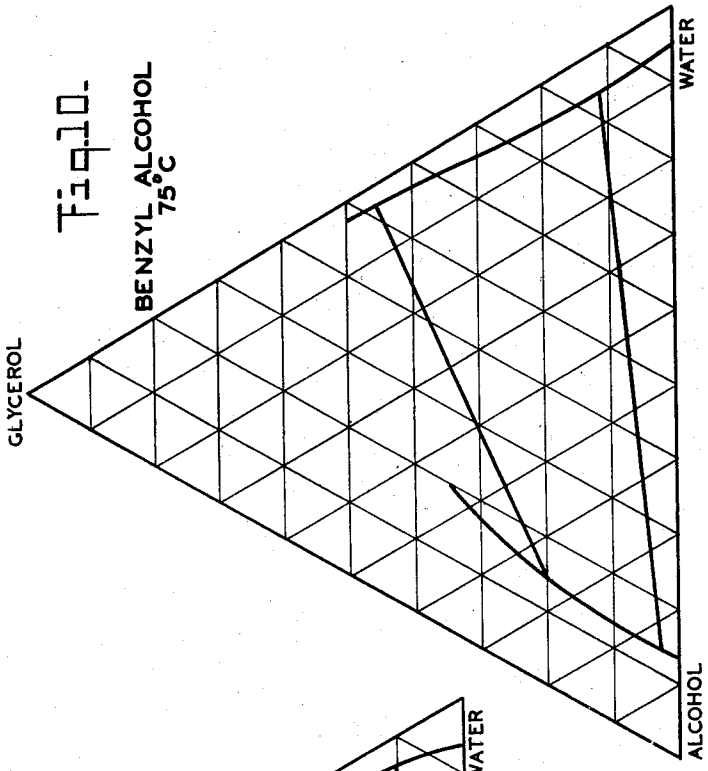
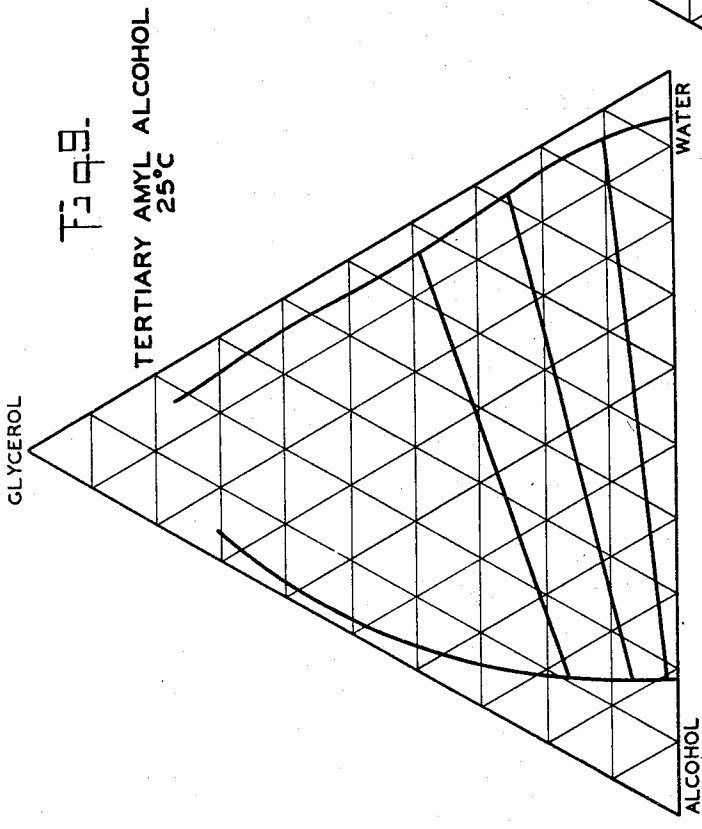


Fig. 9.



INVENTOR.
JOSEPH CLIFTON ELGIN

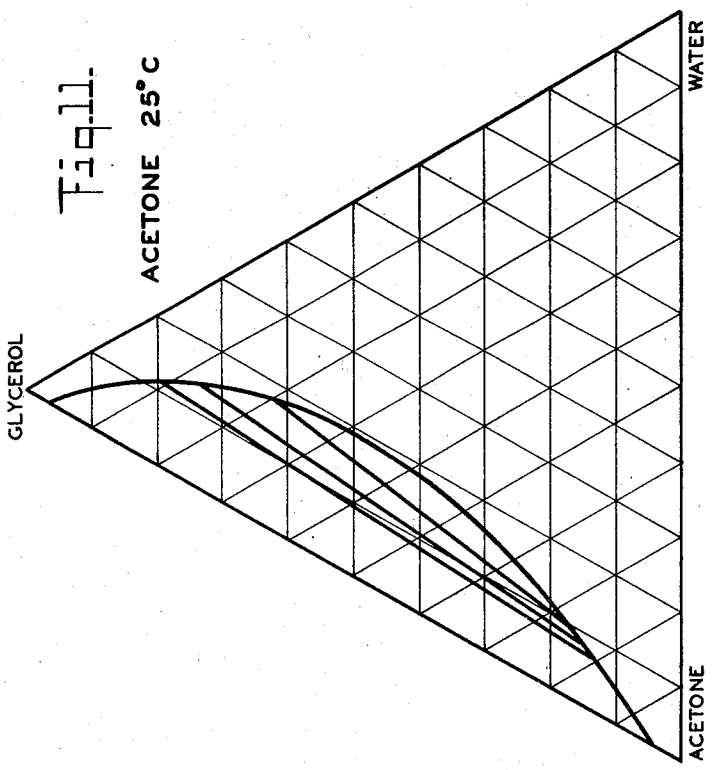
BY Preston Meredith
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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Fig. 11.



INVENTOR.
JOSEPH CLIFTON ELGIN
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GLYCERINE EXTRACTION PROCESS

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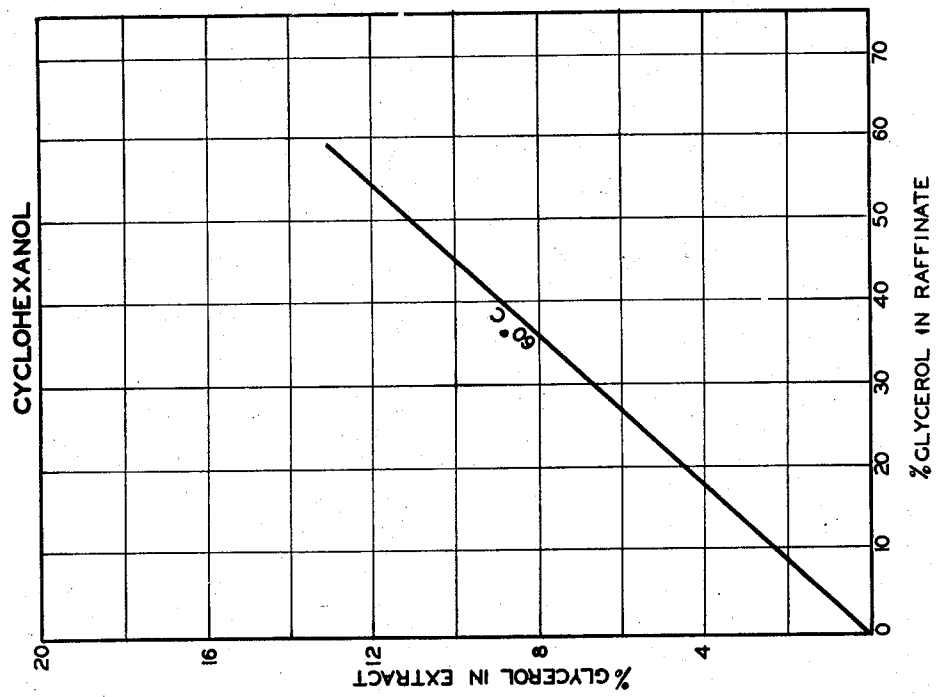


Fig. 12.

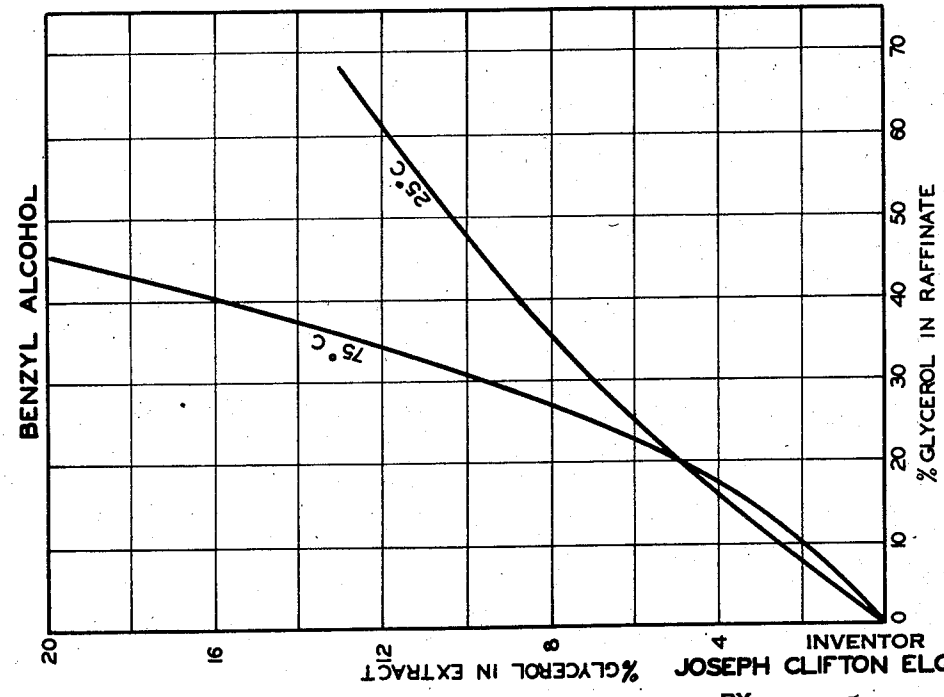


Fig. 12.

INVENTOR
JOSEPH CLIFTON ELGIN
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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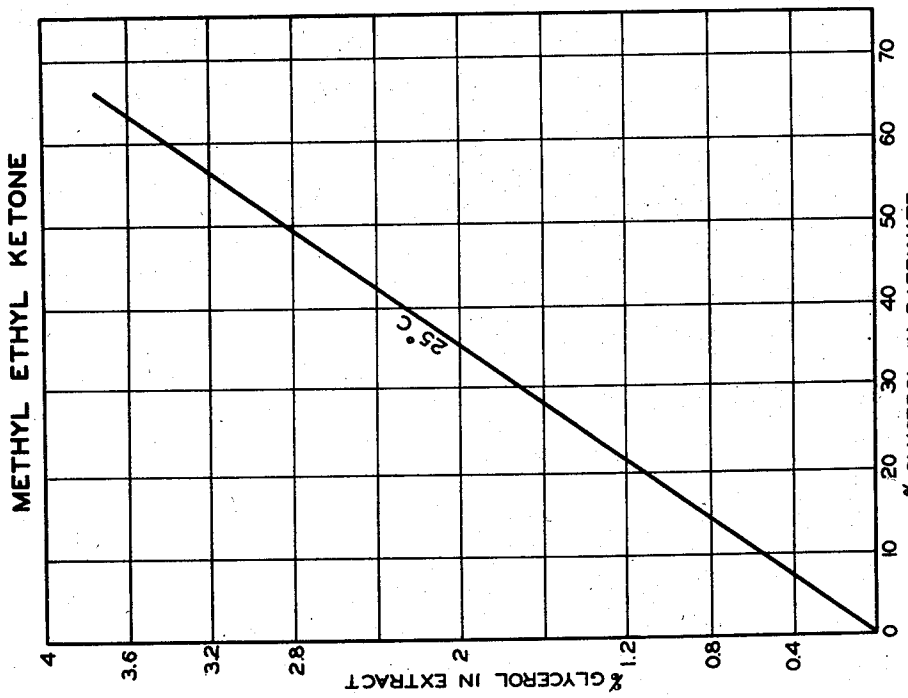


Fig. 15.

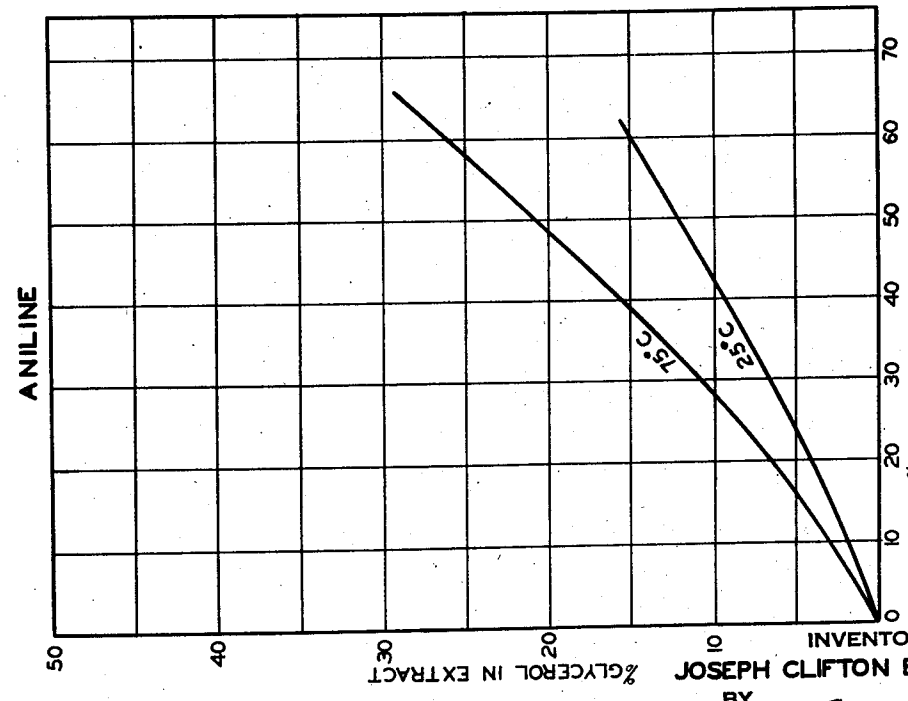


Fig. 14.

INVENTOR
JOSEPH CLIFTON ELGIN
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GLYCERINE EXTRACTION PROCESS

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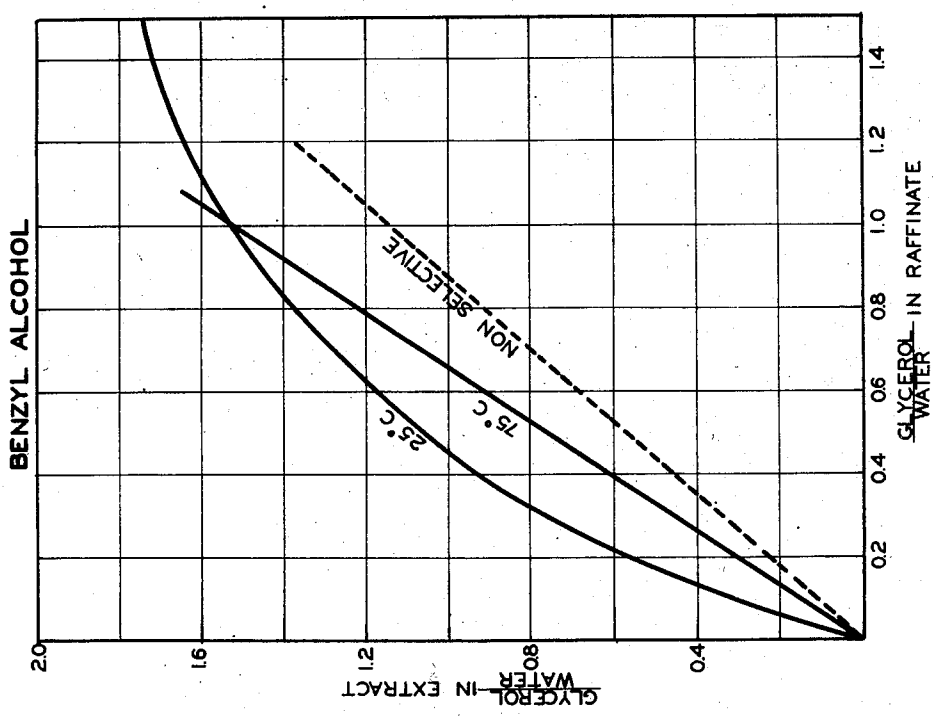


Fig. 17.

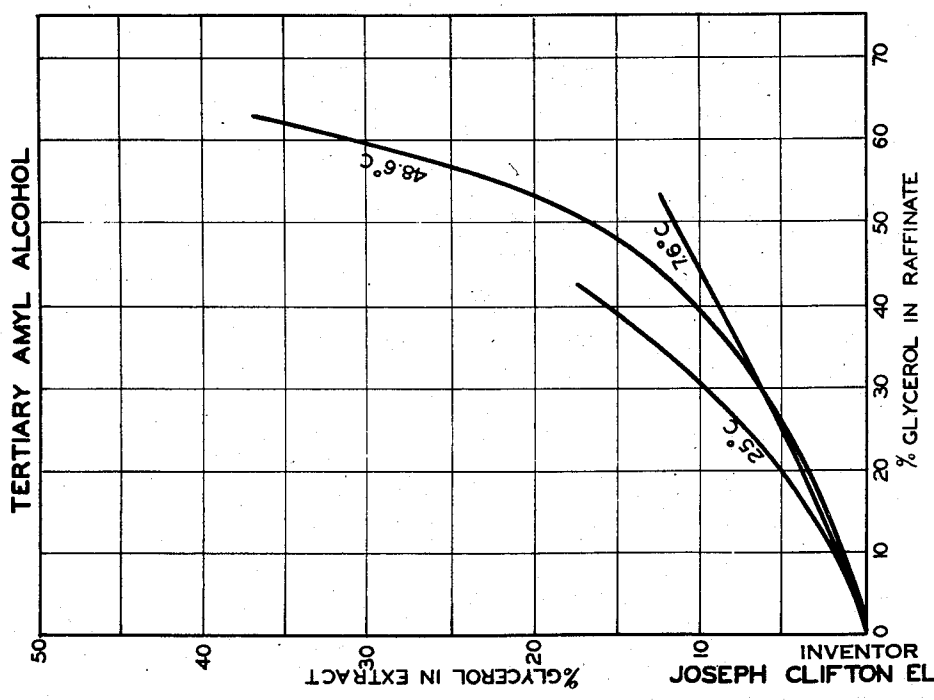


Fig. 16.

INVENTOR
JOSEPH CLIFTON ELGIN
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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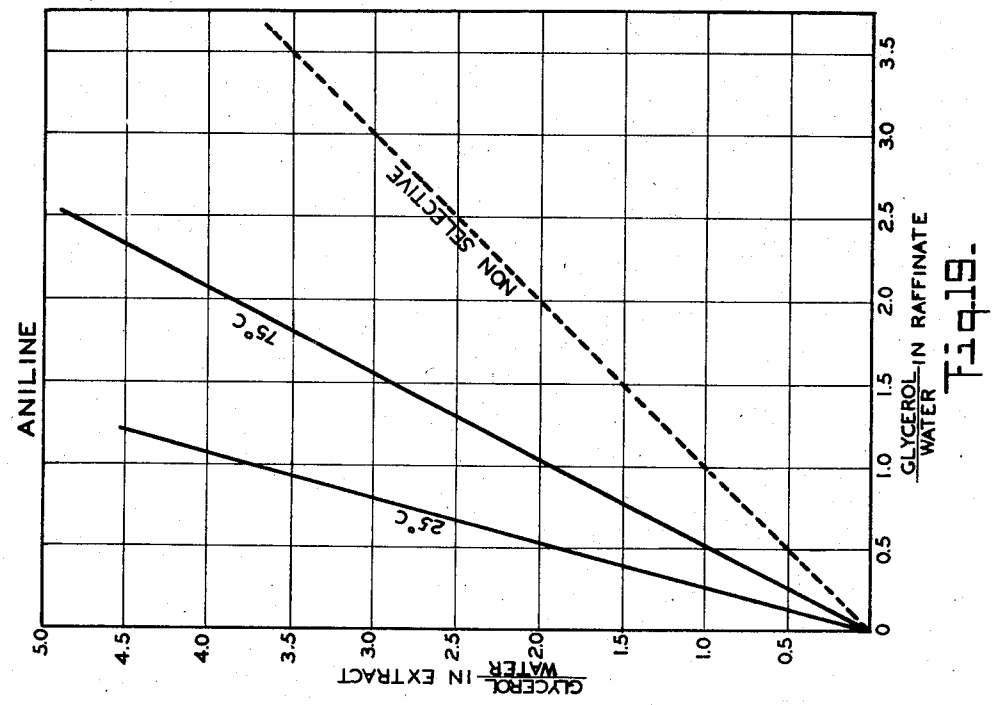


Fig. 19.

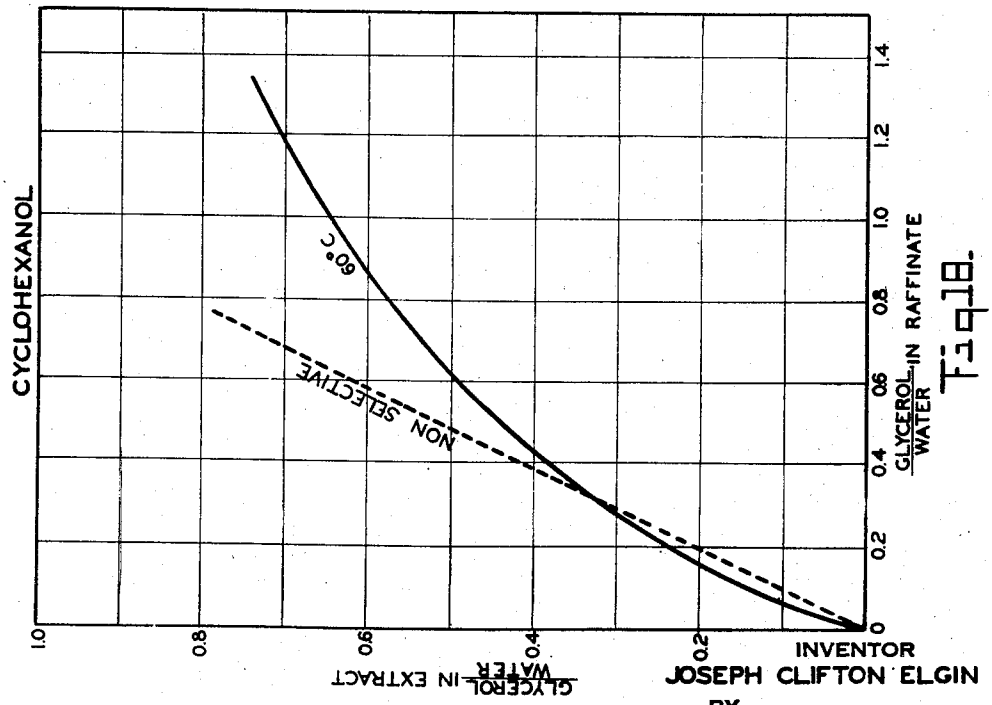


Fig. 18.

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JOSEPH CLIFTON ELGIN
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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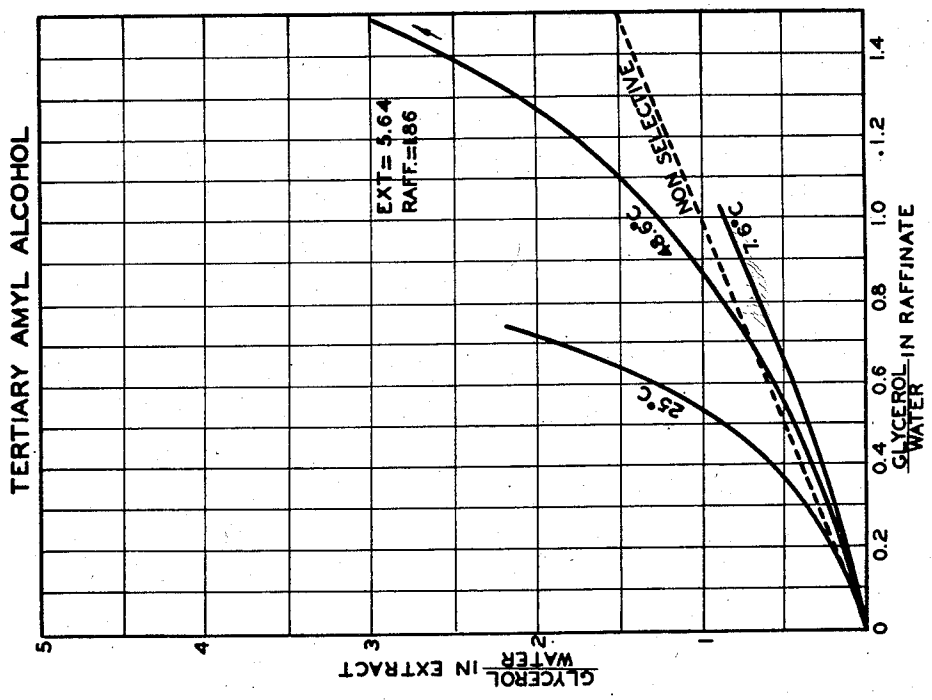


Fig. 21.

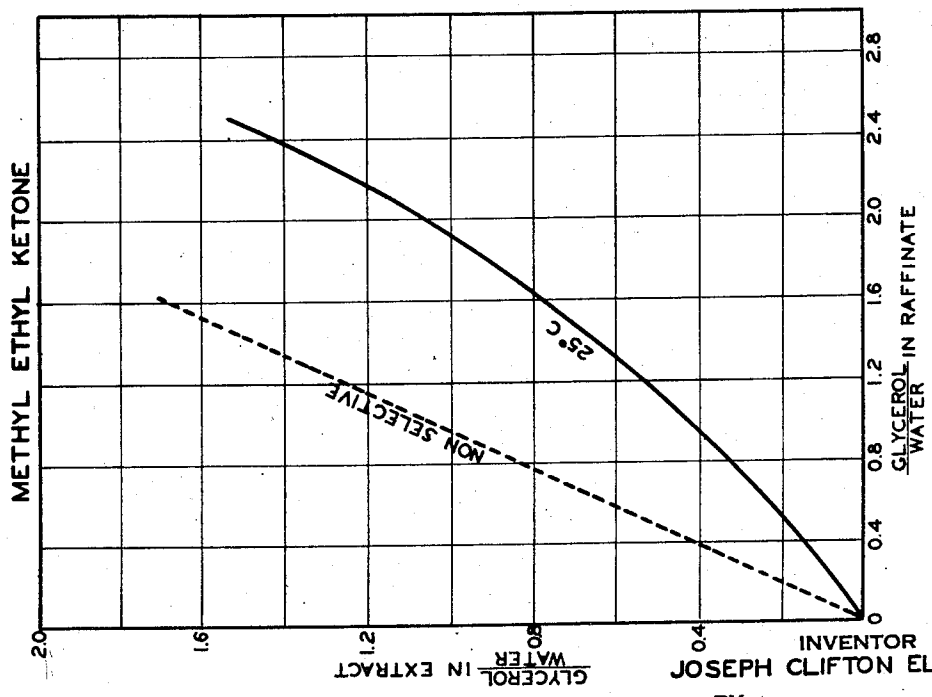


Fig. 20.

INVENTOR
JOSEPH CLIFTON ELGIN
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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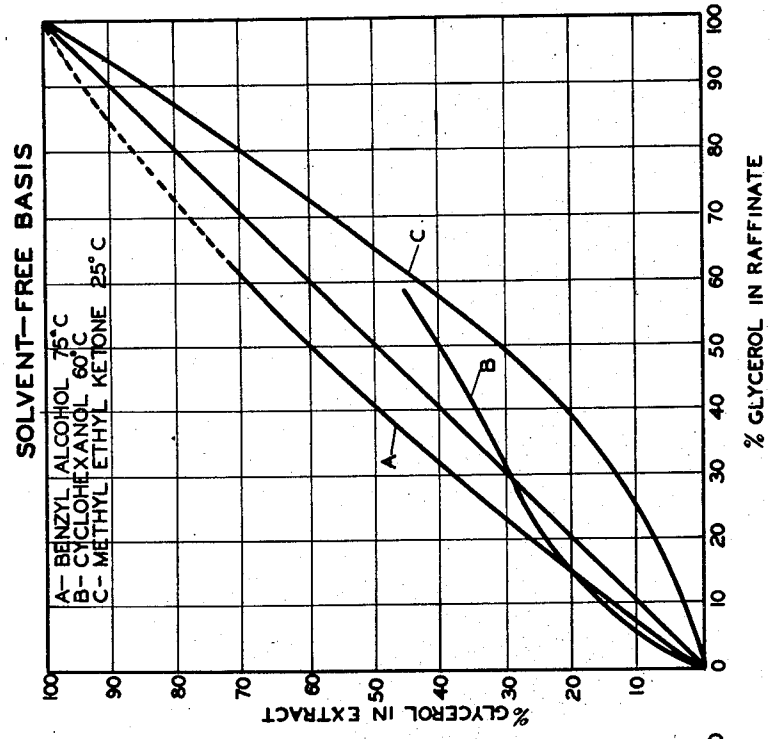


Fig. 22.

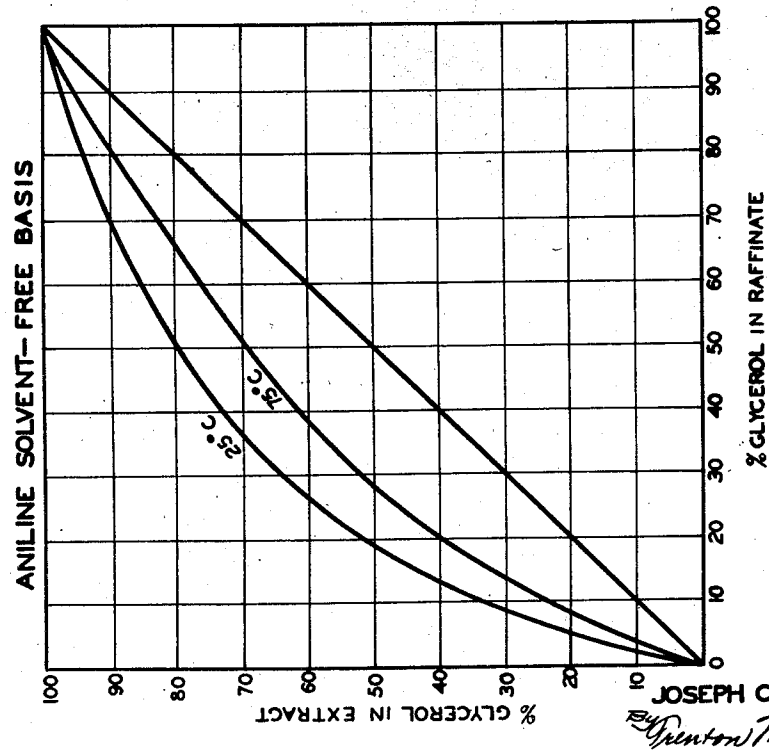


Fig. 22.

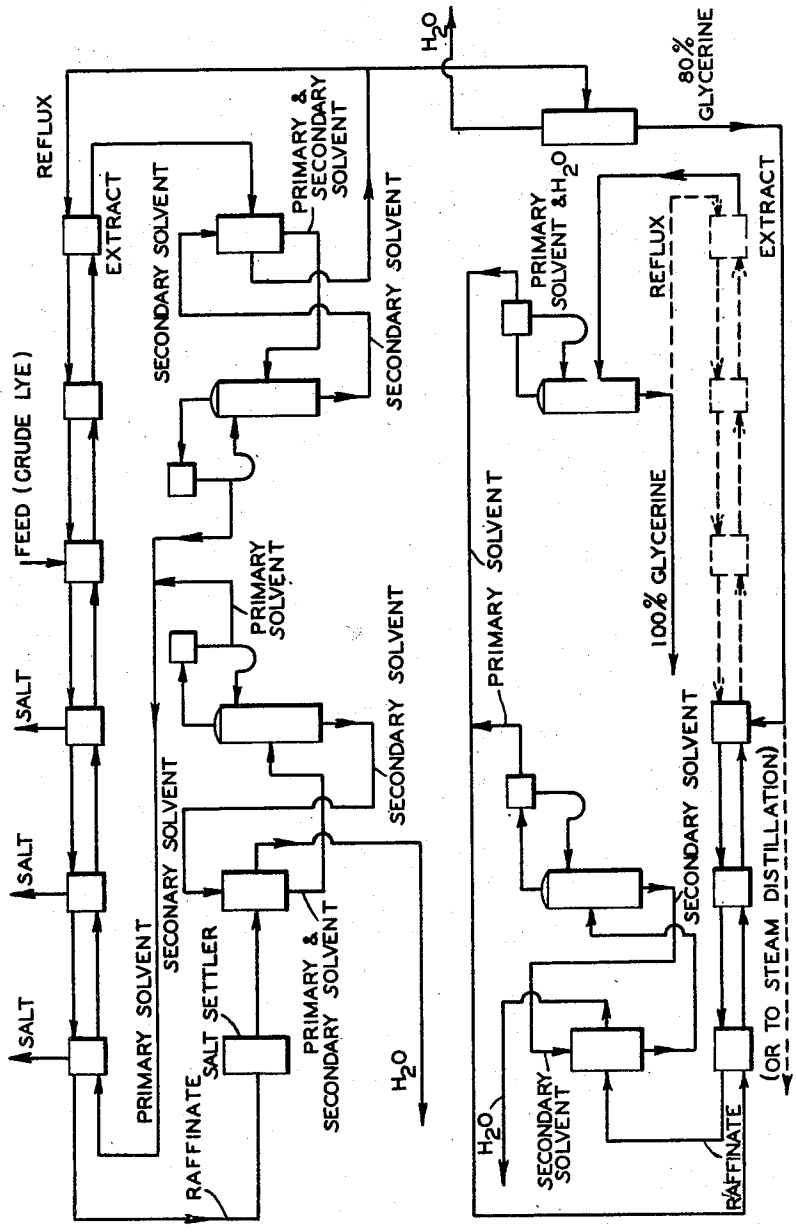
INVENTOR
JOSEPH CLIFTON ELGIN
By Trenton Meredith
ATTORNEY

Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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Fig. 24.



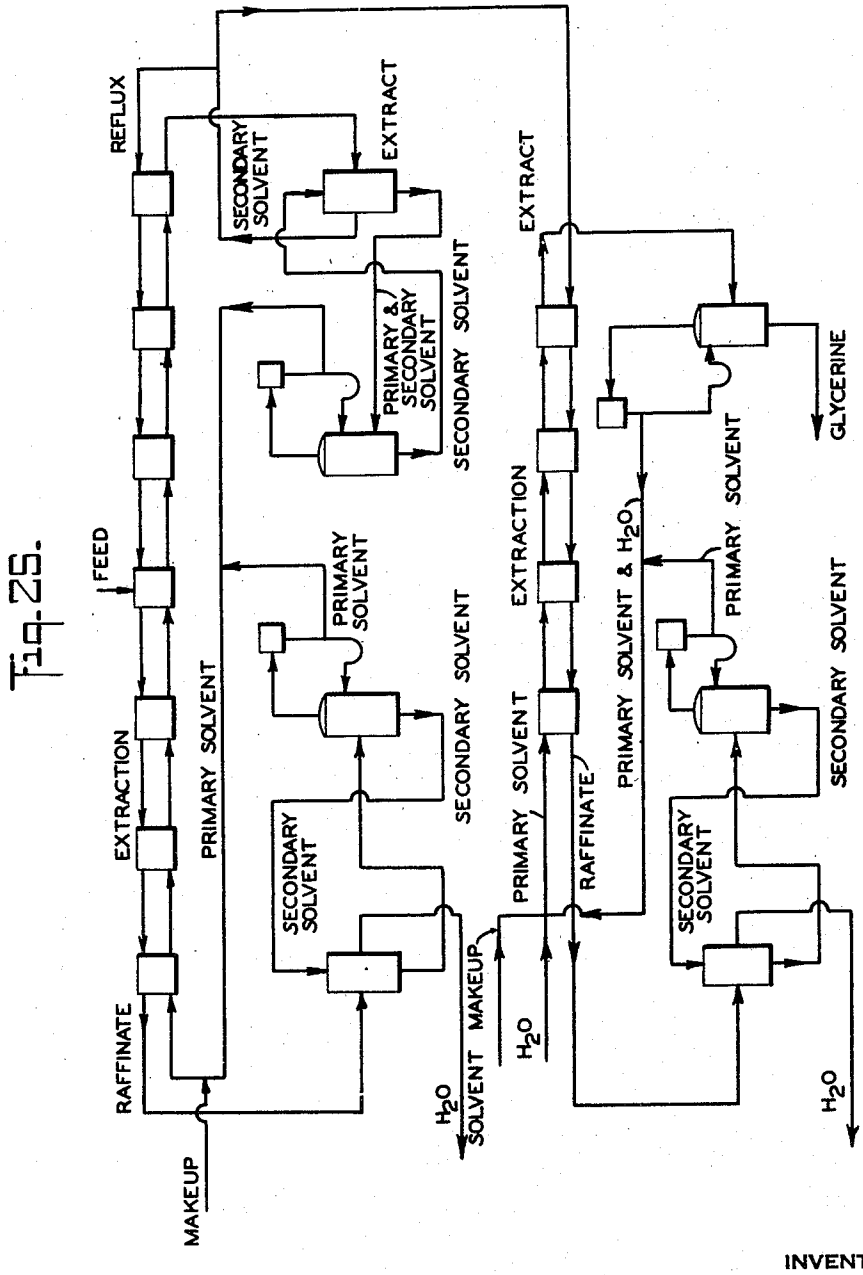
INVENTOR
JOSEPH CLIFTON ELGIN
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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Fig. 25.



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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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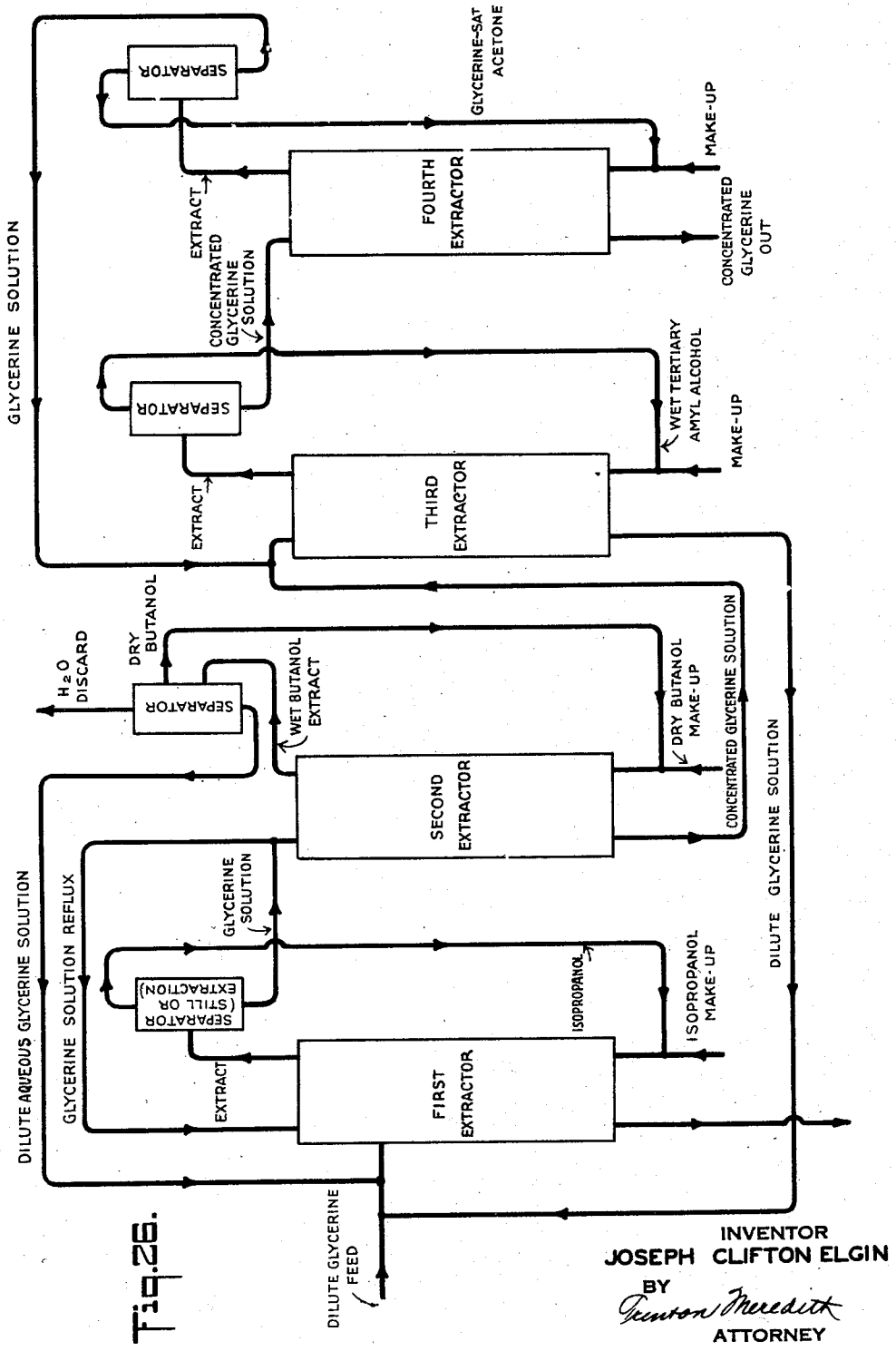


Fig. 26.

INVENTOR
JOSEPH CLIFTON ELGIN
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Trenton Meredith
ATTORNEY

Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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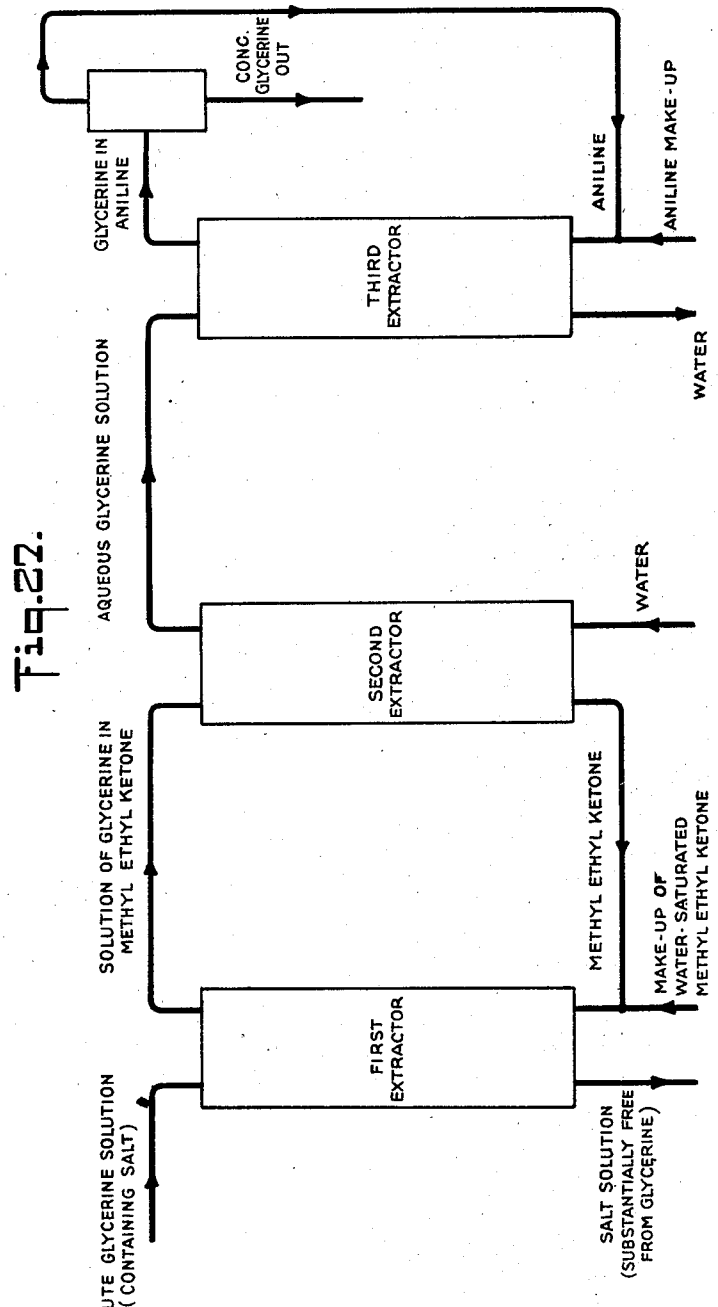


Fig. 22.

INVENTOR
JOSEPH CLIFTON ELGIN
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Pearson Meredith
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Aug. 16, 1949. J. C. ELGIN 2,479,041

GLYCERINE EXTRACTION PROCESS

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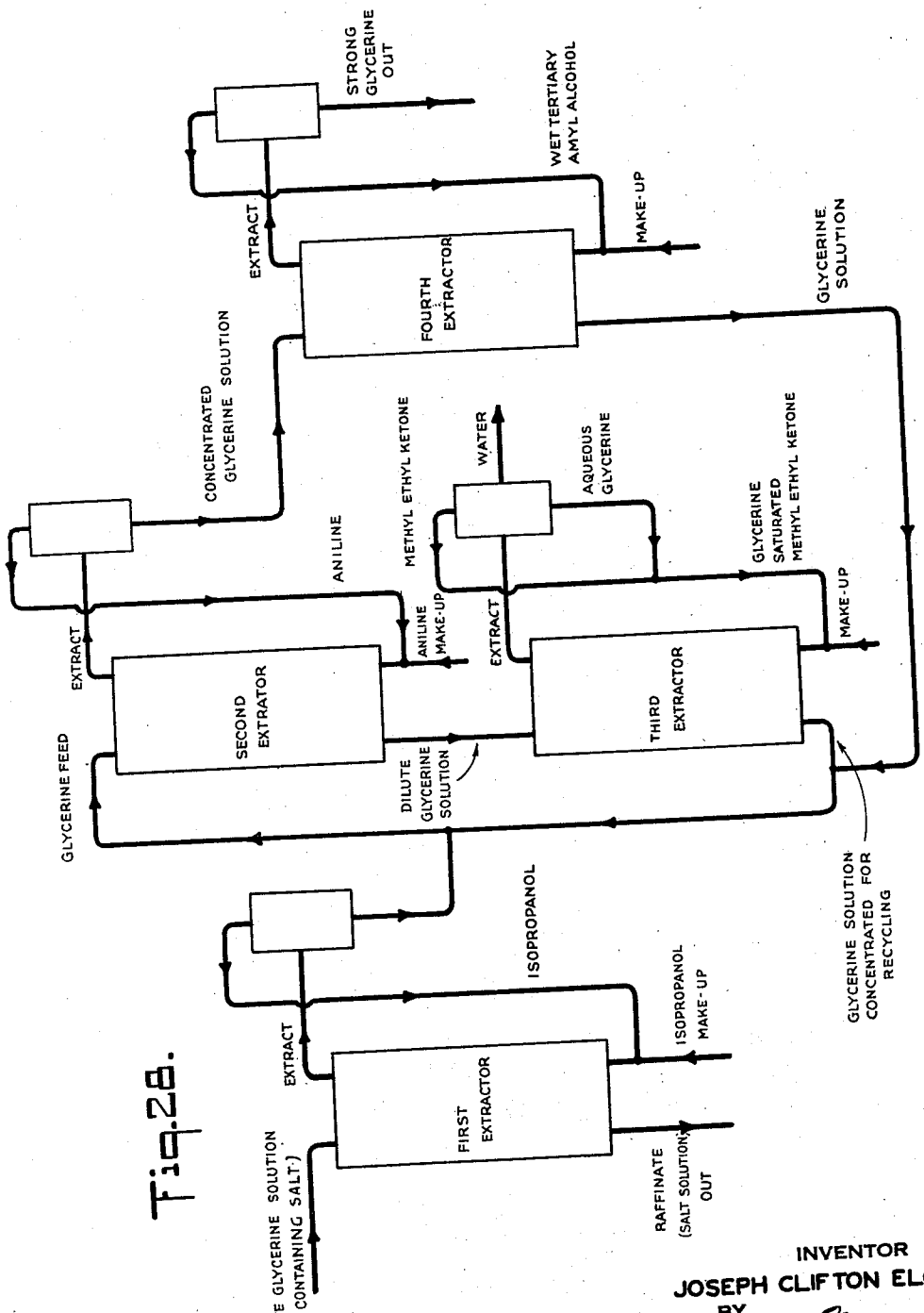


Fig. 28.

INVENTOR
JOSEPH CLIFTON ELGIN
BY Trenton Meredith
ATTORNEY

Patented Aug. 16, 1949 2,479,041

UNITED STATES PATENT OFFICE

2,479,041

GLYCERINE EXTRACTION PROCESS

Joseph Clifton Elgin, Princeton, N. J., assignor to Colgate-Palmolive-Peet Company, Jersey City, N. J., a corporation of Delaware

Application September 18, 1943, Serial No. 502,928

19 Claims. (Cl. 260—637)

1

This invention relates to a method of treating water-soluble polyhydroxy organic materials in aqueous solutions containing the same and is a continuation-in-part of my application Serial Number 349,595, filed August 2, 1940, and now abandoned. More particularly the invention relates to methods of purifying, concentrating, extracting and recovering polyhydric alcohols such as glycerine from aqueous solutions thereof.

There have been vague suggestions in some patented art that glycerine may be purified by means of organic solvents, and in other patents that the glycerine may be separated from associated materials by extraction. In most cases there is no detailed procedure for accomplishing these ends and, generally, the disclosed methods are inoperative to attain the described results. The solvents recited in many cases do not dissolve either the glycerine or the water to a practical extent. Obviously, therefore, substantially no extraction, or practical separation of glycerine and water can take place. Even though two liquid layers may result when contacting aqueous glycerine with such solvents, the ratio of glycerine to water in the solvent is substantially the same as in the water and equal to that of the starting material. Furthermore, the concentration of glycerine in the solvent is very small or negligible. This, of course, does not constitute a separation of glycerine and water, nor a concentration, purification or extraction of glycerine. Such a treatment is a simple dissolving of aqueous glycerine, and its continuation to the maximum limit possible would result solely in dissolving all of the starting mixture in the solvent thereby wholly defeating either the removal of glycerine from water, concentration of the glycerine or purification of the glycerine. Treating aqueous glycerine in such manner and with such solvents that only one liquid layer or phase is formed in the process, even though solids which may be contained therein be precipitated with the formation of a solid phase by the addition of sufficient solvent, likewise does not constitute a separation of water and glycerine, a concentration of glycerine, or an extraction of glycerine in the sense of this invention. Such a process is simple solution of aqueous glycerine, is not a liquid-liquid extraction, and does not come within the scope of this invention. Further, the evaporation of an aqueous glycerine mixture containing solids so that water is thus removed to leave a residue of solids in which a substantially dehydrated glycerine remains absorbed, and subsequently dissolving out this glycerine from the solid residue with solvents, does not constitute separation of water and glycerine or concentration of glycerine by liquid-liquid extraction; such a process is simple leaching and does not fall within the scope of this invention.

2

Even if some of the solvents disclosed in the patented art were employed in liquid-liquid extraction they would be found to dissolve water in a higher ratio to glycerine than the ratio of these materials in the starting mixture. Hence attempts to extract the glycerine into the solvent and recover the glycerine therefrom would result in incomplete stripping, and the solvent phase would contain a lower glycerine content not only in the solvent but on a solvent free basis, that is a less concentrated aqueous glycerine solution. A process operated in this manner would generally be uneconomical.

It has now been discovered that relatively concentrated, pure glycerine may be recovered from aqueous glycerine solutions by means of a solvent or a combination of solvents. The present invention comprises effecting the separation of glycerine and water from a mixture thereof by a liquid-liquid extraction with organic solvents in two or more solvent extraction steps so that two liquid layers or phases are formed in each of the steps in which the glycerine to water ratios are substantially different from each other and from the original mixture of glycerine and water. The glycerine may be concentrated and purified whether the glycerine to water ratio is higher or lower in the solvent phase than in the aqueous phase by the process of the present invention so long as the ratio is different in the two phases and so long as the solvent dissolves a substantial quantity of either the water or the glycerine constituent. In other words, the process is operative if the solvent selectively and preferentially dissolves water or glycerine from the mixture being treated in each of the stages under conditions at which two phases are formed.

The applicant is the first to discover that even though organic solvents which are only partially miscible with water and wholly miscible with glycerine, are contacted with an aqueous solution of glycerine there is nearly always a substantial quantity of water dissolved, in many cases in a higher ratio to the glycerine than in the original mixture, and the glycerine concentration in the total solution is nearly always

lower than in the original mixture. In those cases where a water selective solvent is employed it is usually desirable to recover the concentrated glycerine from the aqueous phase, not the solvent phase.

The applicant is the first to concentrate glycerine in its aqueous mixture and to separate glycerine and water by liquid-liquid extraction with an organic solvent. The applicant is also the first to observe that with certain solvents under certain conditions, there is a mixture, corresponding in principle to a constant boiling mixture in distillation, beyond which the particular solvent cannot effectively extract without some change of extraction conditions. In other words, on one side of this composition the solvent such as tertiary amyl alcohol will selectively extract glycerine, on the other it will selectively extract water, and at the exact composition it is non-selective.

The process in general comprises extracting an aqueous mixture containing glycerine with an organic solvent under such conditions that two liquid layers or phases are formed, one of which layers contains glycerine in proportion to water substantially different from that in the other layer and in the starting material. The layer containing a ratio of glycerine to water higher than that existing in the starting material is then treated with another organic solvent, preferably one more efficient in the concentration range now existing in the starting material, under such conditions that two liquid layers or phases are again formed, one of which liquid layers contains glycerine in proportion to water substantially different from that which obtained in the mixture which served as a starting material for this second liquid-liquid solvent extraction. The result is thereby to remove the glycerine or water or both successively from the original mixture and thus concentrate the glycerine. That is, water may be first removed from the mixture in the extract phase leaving a more concentrated glycerine solution behind which may then be treated with a second solvent in the second stage of the process which preferentially takes glycerine into the extract phase and this extract when separated from the solvent will be a concentrated glycerine. No procedure described in the prior art does such a true glycerine extraction process.

The invention herein described also contemplates the liquid-liquid extraction of crude liquid aqueous glycerine mixtures containing in addition dissolved and/or suspended inorganic and/or organic impurities, such mixtures being derived from any source, for the purpose of obtaining an extracted glycerine of both higher concentration relative to water and containing substantially none or only small quantities of undesirable impurities, such as for example, inorganic compounds, salts and alkalies (e. g. sodium chloride, caustic soda, sodium carbonate and iron acetate), colored bodies, nitrogenous substances, organic salts and fatty acids. While it is usually desired to attain both objects, it is not intended to limit the invention thereto, since it may also be employed solely to concentrate an aqueous glycerine of any degree of purity by preferentially dissolving the water, or the glycerine, therefrom. Or, it may be applied solely for the purpose of extracting and stripping substantially completely a glycerine of greater purity and having, for example, lower salts, caustic and color content, from an impure crude aqueous glycerine

mixture without necessarily effecting a concentration of glycerine thereby.

The invention may be applied to the extraction, purification, and concentration of glycerine in such aqueous mixtures as soap lyes, saponification liquors, or other glycerine containing liquors derived from the hydrolysis of fats and oils in the manufacture of soap and fatty acids, mixtures obtained therefrom by evaporation or other treatment, e. g. crude concentrated glycerines; fermentation liquors and slops derived from the fermentation of molasses or other carbohydrate containing material carried out either for the primary production of glycerine or for alcohols and similar substances; and of crude aqueous glycerine liquors derived synthetically, for example, by the chlorination of propylene and the subsequent hydrolysis or hydrinolysis of the chlorinated hydrocarbon. The process possesses particular merit for the purification of glycerine containing organic impurities having a boiling range near that of glycerine such as the glycerine obtained by distillation from fatty oil soaps e. g. by the process described in Ittner's U. S. Patent Number 1,918,603 and Clayton et al.'s U. S. Reissue Patent Number 19,456. Use of the invention is not, however, limited thereto. While it is proposed to extract usually the glycerine from its mixtures without prior chemical or adsorption treatment or evaporation thereof, it will be understood that chemical or adsorption treatment and/or partial concentration of such mixtures by evaporation or distillation prior to the extraction, so long as there remains a liquid phase, may be carried out without departing from the spirit of this invention. It is possible to employ chemical or adsorption treatment or concentration subsequent to the extraction. The concentration may be effected by any suitable method e. g. as described in Martin H. Ittner's U. S. Patents Numbers 2,164,274; 2,164,275 and 2,164,276.

As previously described if dewatering of aqueous glycerine is the sole objective, the mixture may be extracted with a suitable solvent under such circumstances as fulfill the previously specified conditions so that either water or glycerine is preferentially dissolved by the organic solvent or solvent mixture used in the various steps of the process. In treating crude, highly colored, impure aqueous glycerines which are relatively dilute, that is with a glycerine content between a trace and 50%, it is preferred to separate the glycerine and water therein by extracting with such solvents and in such manner that glycerine is preferentially dissolved and concentrated in the organic solvent layer, thus leaving behind in the aqueous layer the major portion of the colored matter, inorganic substances and other impurities. The solvent solution of glycerine may have lower viscosity, surface tension and salt content than strong and/or crude glycerines and may be cleaned readily by means of absorbent carbon, activated carbon kieselguhr, silica gel or the like. As stated, it has been found in carrying out the extractions with solvents that the colored bodies, inorganic substances, and other impurities normally associated with aqueous glycerine mixtures, such as soap lyes, are extracted to a relatively small or negligible extent, depending upon the circumstances of the extraction, by the organic solvents of the kinds described hereinafter. These impurities remain preferentially dissolved in the aqueous layer especially if this be alkaline since the alkaline impurities are pref-

erentially water-soluble. Conversely, when extracting water from an aqueous glycerine solution in the first step of the process, it is often desirable to have an acid condition in order to favor the solution of the organic impurities in the solvent, leaving a purer non-solvent phase containing concentrated glycerine, inasmuch as the impurities, such as fatty acids, when acid tend to be dissolved preferentially in the solvent phase.

In the preparation of a highly concentrated glycerine from a crude glycerine mixture it has been found particularly advantageous from an economical and practical standpoint to carry out the extraction in two or more distinct and successive steps in each of which is employed a different solvent. The solvent chosen for each of the extraction steps should preferably be one which is best suited for operation with the particular concentration of the glycerine in the aqueous solution being treated in that step. It is of course necessary to select a solvent which will preferentially dissolve water or glycerine depending upon which it is most desirable to remove at the particular stage in the process then in progress. The applicant has found that certain solvents are more successful when used for extracting dilute aqueous glycerine solutions, that is less than 50% and more generally in the range from a trace up to 20 or 30%, whereas other solvents are best suited for extracting the concentrated glycerine solutions, either by removing the remaining few percent of water, where the solvent is water selective, or by dissolving substantially pure glycerine only from the concentrated solution, where the solvent is glycerine selective. Generally speaking, the solvents which are most efficient when working upon the dilute glycerine solutions are fairly satisfactory for the solutions containing from 35 to 65% glycerine although some of the solvents which are very effective for the final purification are also suitable for operation in this middle range of concentrations. It is also possible to use one solvent in the low range of glycerine concentration, a second solvent when the concentration approaches 50% and a third solvent for the final separation. For such an operation, as an example, one might use a water selective solvent with the mixture alkaline to first remove a considerable portion of the water and the impurities, then treat the mixture with a second, glycerine selective solvent which would take a concentrated glycerine solution into the extract phase and finally treat this concentrated glycerine solution with a third solvent, which might be either water selective, to remove the remaining water, or glycerine selective, to dissolve out a pure glycerine from this concentrated solution. It is of course possible and, in some cases, might be more economical to use 4 or even 5 or more extraction steps. However this would be unusual and only justified under extreme circumstances. As a general rule a 2 or 3 step extraction process will prove most economical.

In place of the use of a solvent extraction step for concentrating in one of the steps of a 3 or more step process, it might be advantageous to substitute a distillation operation to concentrate the solution up to the range desired for the next succeeding extraction step. This is particularly true in passing through the range from a dilute glycerine solution containing 35% of glycerine or less to a concentrated glycerine solution containing 65% or more.

An additional feature of the invention, which is of particular advantage for the recovery of glycerine from the raffinate, when using a glycerine selective solvent in one of the stages of the process, is that the raffinate may be washed in a counter-current extraction process with a water selective solvent to such an extent, or in such a manner, that the glycerine-water ratio in the raffinate is the same or substantially the same as in the feed to the original extraction step. The raffinate may then be returned to the mixture being fed into the extractor and re-extracted with the glycerine selective solvent. This feature is of particular advantage in conjunction with the final stages of the process in which the glycerine content of the raffinate from the extraction step may well be fairly large and have considerable value. By treating this raffinate with a water selective solvent the material being removed from the process will be mainly this water selective solvent and the water being carried along therewith. The raffinate is continuously returned to the original counter-current extractor until its glycerine content has been substantially all removed in the extract phase with the glycerine selective solvent. Although this step of recovering the glycerine from the raffinate portion of an extraction step is preferably of advantage when dealing with a concentrated glycerine solution, it may be used in any stage of the process where a glycerine selective solvent is used in the extraction and it is undesirable or uneconomical to use this glycerine selective solvent in a sufficient proportion to strip the feed to the extractor of its glycerine content. The mode of operation of such a raffinate extraction step may be more fully understood by a study of the flow sheets of Figure 28 and Example 5.

In the investigations and extractions of aqueous glycerines, the following solvents have been found to be among those suitable for use in this invention: aliphatic alcohols containing more than two and preferably less than eight carbon atoms, e. g. n-, iso-, sec-, and tert.-butanols, n- and iso-propanol, methyl butanol, ethyl butanol, n-, iso-, sec-, and tertiary amyl alcohol, methyl amyl alcohol, hexanols; aromatic alcohol, e. g. benzyl alcohol; cyclic hydroxy compounds, e. g. cyclohexanol, methyl cyclohexanol, phenol, cresol, ortho amyl phenol, guaiacol; aliphatic, aromatic and cyclic amines, e. g. triethylamine (water miscible at low temperature, partially immiscible high temperature), aniline, quinoline, picolines; and ketones, e. g. acetone, methyl ethyl ketone (water miscible at very low and high temperatures, partially miscible at medium temperatures), and methyl isobutyl ketone. It will be understood that the invention is not limited to those solvents named, but that one may employ as solvent any organic liquid which forms two liquid layers with the aqueous glycerine mixture, which results in one or the other of the liquid layers containing glycerine in ratio to water higher than the other layer or than the starting mixture, and which solvent, if mixed with either one or the other of the two pure components, glycerine or water, in the absence of the other, dissolves at least 4% of that component which it selectively extracts from tertiary mixtures with both of the components. Other solvents both of the above preferred class and of different classes, for example, certain ethers e. g. glycol monobutyl ether, dioxane, propylene oxide, diglycol monobutyl ether, mannitan, tetrahydrofurfuryl alcohol, furfuryl alcohol; certain esters e. g. monoacetin, diacetin, glycol monobutyrate, butyl lactate, n-propyl lactate and

isopropyl lactate; and certain aldehydes, e. g. propionaldehyde may be also employed. Isomeric compounds such as the butyl and amyl alcohols show individual characteristics and differ in their usability and ability to separate water and glycerine varying between the isomers.

The solvents listed in the paragraph above are all of value in carrying out the different stages of the process but they vary among themselves in their suitability for working upon glycerine and water solutions, depending upon the concentration of the particular solution in which they are to be used as the extraction medium. Likewise these solvents vary among themselves as to whether they are water selective or glycerine selective. In some cases the solvents may be water selective at one temperature and the same solvent be glycerine selective at another temperature. An example of a solvent of this latter type is tertiary amyl alcohol. Furthermore, the suitability of the individual solvents is influenced by the presence of additional impurities in the glycerine-water mixture being extracted. Among the solvents which I have found particularly suitable for working with dilute glycerine solutions are propanol, isopropanol, dioxane, tertiary butyl alcohol and n-butyl alcohol. Of these solvents isopropanol and tertiary butyl alcohol are particularly useful when treating dilute glycerine solutions which contain substantial amounts of salt impurities. In the case of dilute glycerine solutions free from any considerable amounts of dissolved salts, aniline has been found very useful. Examples of solvents which have been found especially suitable as finishing solvents for treating the concentrated glycerine solutions are tertiary amyl alcohol, methyl ethyl ketone and acetone. Of these three solvents the first is glycerine selective while the last two are water selective. Examples of solvents which are useful for treating glycerine solutions containing from 30 to 70% glycerine are benzyl alcohol at elevated temperatures, aniline, and cyclohexanol (water selective).

The solvents may be used singly or a mixture of solvents may be used in any of the extraction stages. Obviously in using a mixture of solvents, the solvents being mixed must have similar or a desirable combination of properties which would render the use of the mixture advisable. That is, one would not mix under ordinary circumstances a water selective and a glycerine selective solvent to be used as a common mixture in a single extraction step. While it might be possible with such a mixture, depending upon the proportions used and the relative selectivity of the two solvents, to gain a certain concentration of the glycerine solution, nevertheless the two solvents would be working in opposition to each other rather than cooperating in the extraction step. By the use of solvent mixtures, in which the solvents have similar properties in regard to being glycerine or water selective, on the mixture being treated and at the temperature involved, it is frequently possible to take advantage of other desirable properties of the solvents. Any of the above solvents may be used dry or they may be used partially or completely saturated with glycerine or water depending upon whether they are to extract water or glycerine.

Examples of possible combinations of these solvents which can be used as mixtures are:

1. A combination of at least two water selective solvents, forming at least partially immiscible phases with aqueous glycerine, e. g., n-butyl alcohol and tertiary amyl alcohol (at low temperatures); n-butyl alcohol and cyclohexanol (at high concentrations and temperatures); acetone and n-butyl alcohol; acetone and methyl ethyl ketone; methyl ethyl ketone and tertiary amyl alcohol (at low temperatures); or mixtures of these combinations operative at the same temperatures.

2. A combination of at least one water selective solvent and a water immiscible solvent selective for the first solvent (and preferably also for water), e. g., includes most of those of the first group plus combinations of the following types: acetone and triacetin; acetone and benzene; n-butyl alcohol and triacetin; or mixtures of these which are operative at the same temperatures. This includes mixtures of at least one substantially glycerine immiscible, water miscible solvent such as acetone or methyl ethyl ketone, and a solvent wholly or partially immiscible with water but completely miscible with glycerine such as n-butyl alcohol, tertiary amyl alcohol (at low temperatures), cyclo-hexanol (at high concentrations and temperatures). The second solvent may also be essentially immiscible with glycerine and water.

3. A combination of at least two glycerine selective solvents, forming at least partially immiscible phases with aqueous glycerine, e. g., tertiary butyl alcohol and/or isopropanol with tertiary amyl alcohol (at higher temperatures and concentrations); aniline and tertiary amyl alcohol (at higher temperatures and concentrations); isopropanol and tertiary amyl alcohol (at higher concentrations and temperatures); aniline and tertiary butyl alcohol; or mixtures thereof which are operative at the same temperature.

4. A combination of at least one glycerine selective solvent whether or not wholly or partially miscible with water, and a water immiscible solvent selective for the first solvent (and preferably also for glycerine), e. g., includes most of those of the third group plus combinations of the following types: isopropanol and toluene; isopropanol and kerosene; dioxane and triacetin; tertiary butyl alcohol and benzene; or mixtures of these which are operative at the same temperatures.

Less desirable combinations of solvents include those in which one or more dry solvents are water-selective, and one or more dry solvents are glycerine selective, e. g., cyclo-hexanol and tertiary amyl alcohol at higher temperatures.

It is also within the scope of the invention to use mixtures of three or more solvents so adjusted in composition that the salt content of the extract is held down where salt is contained in the aqueous feed, the desired degree of miscibility-immiscibility is obtained, and glycerine or water is selectively removed.

Among the other novel variations in the type of solvent or solvent mixture employed in the various stages of the process are the following:

Using at least one water miscible solvent selective for glycerine and sufficient soluble ionizing materials such as sodium chloride, sodium hydroxide, sodium carbonate, sodium sulphate or other alkali or salts to form immiscible layers at the operating temperatures and concentrations, e. g., isopropanol, dioxane, triethylamine (at low temperatures), or mixtures thereof;

Using at least one solvent which is not wholly miscible with the glycerine or with water, e. g., methyl ethyl ketone (at low temperatures). With solvents of this type which dissolve substantial

amounts of the glycerine and/or water, it is possible to separate completely the glycerine and water by means of reflux;

Using at least one partially water immiscible solvent whether water or glycerine selective, or mixtures thereof, which is diluted or saturated with water in order to extract the glycerine from an aqueous glycerine, e. g., water saturated n-butyl alcohol; water saturated benzyl alcohol; water saturated mixtures of n-butyl alcohol and tertiary amyl alcohol. When employing a water saturated water selective solvent alone, the resulting solvent solution of glycerine has the water in a greater ratio to the glycerine than the original feed so that only purification and exhaustion takes place;

Using at least one partially glycerine immiscible solvent whether water or glycerine selective or mixtures thereof, which is saturated with glycerine in order to strip water from the glycerine, e. g., glycerine saturated acetone, and/or glycerine saturated methyl ethyl ketone.

In separating glycerine and water, extracting and concentrating glycerine with organic solvents it is possible to vary the conditions of the extraction, e. g., temperature, quantity of solvent employed, the number of contacts between the solvent and the aqueous glycerine phase. Any known type of equipment and mechanical details of operation may be employed. The extraction may be intermittent or continuous, as is best adapted to secure the most efficient technical and economic results. In employing columns it is possible to use unpacked or packed towers and/or to employ plates or baffles therein. It is possible to pass the solvent or the disperse phase through the aqueous layer or to pass the aqueous layer through the solvent. Settling areas may be provided at the top or bottom of the columns or suitable settling chambers may be provided outside the tower. Centrifugal means may be provided for accelerating separation of the phases from either the continuous or multiple stage extraction systems. The nature of the aqueous glycerine under treatment, the conditions of operation, and other factors incuding the relative cost of equipment as compared with power costs, will affect the type of equipment and method of extraction to be employed.

While normally, it is preferred to extract at temperatures between about 15° C., and appreciably below the boiling point of any of the solvents, usually ordinary room temperature, one may regulate and employ temperatures above the boiling point of the solvents by the use of pressure, or refrigerate to low temperature. Ordinarily, it is preferred, for example, to extract with tert-amyl alcohol at roughly 25° C., but in extracting aqueous glycerine of approximately 50% glycerine content or higher one may use temperatures of roughly 50° C., and higher depending upon the circumstances. With aniline as the solvent it is preferred to use a temperature in the vicinity of 75° C., or above; with benzyl alcohol, about 25° C.; with propanols a temperature between room and their boiling point.

It will be understood that the percentage extraction of glycerine and the concentration of the glycerine in the extract resulting from a single contact with a specified quantity of solvent is not complete and is limited by an equilibrium distribution between the two layers which depends on such conditions as concentration, temperature, and the particular solvent. In other words a nearly complete recovery of glycerine or separation of water and glycerine is usually not obtainable in a single contact. While one may reduce the glycerine (or water content as the case may be) of the aqueous layer to a low degree and obtain a high percentage removal of glycerine in a single contact or a multiple series of simple contacts with fresh solvent, this usually requires a much larger quantity of solvent and hence quantity of heat to remove it from the extract than it is usually desirable to employ. Further, it results in a lower concentration of glycerine relative to water in the extract than it is usually desirable to obtain. It is therefore preferred in practice, in order to obtain a high percentage recovery of glycerine and at the same time greatly reduce the quantity of solvent necessary and increase the concentration of glycerine relative to water and solvent in the solvent layer, to extract countercurrently in a multiple series of contacts, or countercurrently and continuously. In this way the quantity of solvent may be so adjusted in relation to the number of contacts as to obtain the desired percentage recovery of glycerine under any specified circumstances in the maximum possible economic and efficient manner.

When desired, in order to increase the concentration of glycerine or water in the solvent layer beyond that which is in equilibrium with the feed, it has also been found possible to return a portion of the more concentrated extract, either glycerine or water depending upon the selectivity of the solvent from which solvent has been removed, to the extract end of the system as reflux. In such cases the feed of aqueous glycerine is at some intermediate point in the extraction system. The proportion of reflux must be reasonable in order to economically operate the process and in any event it must not be greater than that amount which causes complete miscibility in the last stage of the extraction.

It may also be desirable to have the salt or alkali content of the extracted glycerine lower than that obtained in equilibrium with the original crude feed. To do this it is possible to return a small portion of the solvent-free extract to the extraction system to reflux such substances down to the aqueous residue and thus reduce the quantity of such inorganic substances in the glycerine extract. To accomplish this salt removal in a counter-current process the solvent is fed into the extraction apparatus at one end, the feed at an intermediate point and a portion of the extract after it has been freed from solvent is returned to the end of the extractor opposite to the solvent inlet end so that the purified glycerine flows countercurrent to the solvent and in the same direction as the feed. The point in the extractor wherein the crude mixture is admitted is that at which the salt content of the feed mixture is the same as the glycerine extract being extracted by the solvent. For a showing of the operation of such a reflux system to wash out the salt impurities, see the flow sheet in Figure 26 and Example 3, particularly the discussion of the operation of the first extractor.

This principle of reflux in solvent extraction may be applied to any of the procedures herein described and is not limited to the examples given above by way of illustration only.

It has also been found advantageous to employ the solvent partly or fully saturated with water in order to assist in stripping the glycerine from the residue. Where employing water selective, glycerine immiscible solvents, such as acetone or methyl ethyl ketone, the solvent may be

saturated with glycerine, and water substantially free of or just saturated with solvent may be refluxed.

In the drawings, Figures 1 to 11, inclusive, are charts based on extensive experimental data which may be used to determine the selectivity of the solvents; the range of compositions of tertiary mixtures of glycerine solvent, and water within which operation is possible, the proportion of, and the concentrations in, the various phases, extracts and residues; the maximum glycerine to water ratio obtainable with reflux or without reflux and a given feed; the number of stages necessary to effect a particular separation; the quantity of solvent required to obtain the desired degrees of extraction; and various other data. In order to discuss the importance and necessity of these curves, the chart for tertiary amyl alcohol at 48.6° C. (Figure 1), will be considered in detail but the remarks apply with equal weight to the other charts.

As may readily be seen, the glycerine is completely miscible with the alcohol and with the water but it is not miscible completely with all mixtures of these two. Only mixtures falling within the area marked out by the curve will separate into two layers. One of these contains a larger amount of water in proportion to solvent, and the other a larger amount of solvent in proportion to water. The proportion of these two phases as well as the concentration thereof may be determined by the tie lines extending between the sides of the binodal curve across the area of immiscibility. For example, a mixture of 25% tertiary amyl alcohol and 75% of a 69% aqueous glycerol (i. e., 25% tertiary amyl alcohol, 52% glycerol, and 23% water) falls within the area of immiscibility and will separate into two phases. The composition of the two phases is determined by the extremities of a tie line A—B passing through that point, which shows the solvent phase to contain 59% alcohol, 35% glycerol and 6% water (i. e., 59% alcohol and 41% of an 85% glycerol). The aqueous phase contains 6% alcohol, 61% glycerol and 33% water (i. e., 6% alcohol and 94% of 65% glycerol). In other words, the aqueous glycerol is much more highly concentrated in the solvent layer than in the aqueous layer, and the solvent is glycerine selective under these conditions of operation. This can be established by extending the tie line A—B toward the left, and determining that it cuts the solvent-glycerine axis rather than the solvent-water axis. If it cuts through the solvent corner it is not selective and if it cuts through the solvent-water line it is water-selective. It will be observed that from the tie lines shown, at higher concentrations at 48.6° C., tertiary amyl alcohol is glycerine-selective. At about 41% glycerol, it is non-selective and at lower concentration it is water-selective. The proportion of solvent layer to water layer is determined by the ratio of line XB to line XA. The actual quantities of each may be calculated from the known charges and composition of the layers. The maximum glycerine (or water) separation obtainable with a given feed and without reflux, employing countercurrent extraction to best efficiency is determined by drawing a line from the glycerine feed concentration on the glycerol-water axis to the solvent corner of the diagram. At the intersection of this line with the side of the binodal curve representing the aqueous phase, a tie line is drawn. At the point of intersection of this tie line with the solvent phase portion of the curve is the concentration of the extract in equilibrium with the aqueous phase at the point of feed. A line drawn from the solvent corner through this point will intersect the glycerine-water side of the triangle at the maximum concentration obtainable from the extract without reflux. The maximum concentration of the aqueous glycerine obtainable from the extract with reflux is found by drawing a line through the solvent corner tangential to the curve, and where it strikes the glycerine-water axis is the maximum concentration of aqueous glycerol obtainable with the solvent.

In operating the extraction process on a feed of given composition, the quantity of solvent which is required to obtain a specified recovery of the glycerine in this feed depends upon the number of contacts employed, or vice versa, with a specified quantity of solvent and number of stages, the degree of recovery obtainable will be fixed. With counter-current multiple contact operation, the maximum concentration of extract as pointed out above is theoretically obtainable together with complete recovery if the quantity of solvent be sufficient which is not the case in simple multiple contact operation. The maximum quantity of solvent which need ever be employed occurs for single contact operations and this cannot exceed the quantity limits fixed by the miscibility region of the phase chart. With a specified quantity of solvent, the degree of recovery of glycerine is improved as the number of contacts is increased, but there is a limiting degree of recovery for a fixed extract concentration beyond which one cannot go with this quantity of solvent even though an infinite number of contacts is employed. If substantially complete recovery is desired, there is a minimum quantity of solvent with which this can be accomplished. In practice the quantity of solvent utilized will depend upon the number of contacts which it is desired to use. Any of these factors can be calculated from the phase charts by the method of Hunter and Nash (J. S. C. I. 53, 95T, 1934).

The diagrams or charts of Figures 2 to 11, inclusive, represent the ternary systems employing other solvents and/or other temperature conditions.

In the drawings, Figures 12 to 16, inclusive, are distribution charts showing the distribution of glycerine between the raffinate and the extract phase in a solvent extraction of aqueous glycerine solutions of various concentrations. The figures identify the solvent used and the temperature at which the extraction was carried out as follows:

Figure 12—Benzyl alcohol at 25° C., and 75° C.
Figure 13—Cyclohexanol at 60° C.
Figure 14—Aniline at 25° C., and 75° C.
Figure 15—Methyl ethyl ketone at 25° C.
Figure 16—Tertiary amyl alcohol at 7.6° C., 25° C., and 48.6° C.

The data from which these charts were prepared was obtained by carrying out simple batch extractions with the various solvents at the temperatures named. Various proportions by volume of the respective solvent and aqueous glycerine solution were used. The mixture of solvent and solution was agitated for considerable time until thoroughly intermixed, and the solvent and raffinate layers allowed to stratify. Samples from the extract phase and the raffinate phase were analyzed for their glycerine content. The results were plotted as the per cent of glycerine in the extract against the per cent of glycerine in the raffinate.

In the distribution charts the extract phase includes the solvent which is a major constituent. In order to show the concentrating effect of the solvent, the curves shown in Figures 17 to 21, inclusive, were plotted. These charts, which are hereinafter designated as selectivity charts, show the glycerine to water ratio in the extract and raffinate phases. That is, where the ratio of glycerine to water is 0.5, a 33⅓% glycerine solution in water is present; where the ratio is 1.0, the solution has a 50% concentration; where the ratio is 2.0, the solution has a 66⅔% concentration, etc. In order to obtain the data for preparing these charts, it was necessary to analyze the samples from the various phases for their water content as well as their glycerine content.

The figures identify the solvent used and the temperature at which the extraction was carried out in the same manner as Figures 12 to 16, as follows:

Figure 17—Benzyl alcohol at 25° C. and 75° C.
Figure 18—Cyclohexanol at 60° C.
Figure 19—Aniline at 25° C. and 75° C.
Figure 20—Methyl ethyl ketone at 25° C.
Figure 21—Tertiary amyl alcohol at 7.6° C., 25° C. and 48.6° C.

As an aid in studying these charts, a dotted line, designated "non-selective" is drawn to show where the extract and raffinate phases consist of glycerine solutions of the same concentration. Where the curve is above and to the left of this "non-selective" line, the solvent is being used under conditions wherein it is glycerine-selective. Where the curve is below and to the right of the line, the solvent is being used under conditions wherein it is water-selective.

Figure 22 shows the concentration in per cent of glycerine in the extract on a solvent free basis, plotted against the per cent of glycerine in the raffinate, for aniline.

Figure 23 is a chart prepared in the same manner as Figure 22, but gives a comparison of the selectivity of benzyl alcohol at 75° C., cyclohexanol at 60° C., and methyl ethyl ketone at 25° C.

Figure 24 is a flow sheet for the extraction process described in Example 1.

Figure 25 is a flow sheet for the extraction process described in Example 2.

Figure 26 is a flow sheet for the extraction process described in Example 3.

Figure 27 is a flow sheet for the extraction process described in Example 4.

Figure 28 is a flow sheet for the extraction process described in Example 5.

The following examples are illustrative of the glycerine extraction process carried out in a plurality of extraction stages using different solvents in each extraction stage:

Example 1

Referring to Figure 24, the crude feed, e. g., a soap lye containing about 10% glycerine is extracted countercurrently at a temperature between room and about 75° C., in multiple stages (or if desired, continuously) with a primary solvent, such as isopropyl alcohol, that forms consolute mixtures with both glycerine and water but is only partially miscible with glycerine-water mixtures containing the concentration of dissolved salts present in the feed. Other solvents such as n-propyl or ter. butyl alcohol or their mixtures may be similarly used. The incoming alcohol solvent fed to the extraction system may be dry but preferably contains a certain proportion of water in order to assist the stripping of the glycerine from the aqueous residue leaving the primary extraction stage, and reducing the number of contact stages required, provided that the quantity of water present in relation to the dissolved salts content is not sufficient to render the solvent completely miscible with the aqueous layer leaving. The solvent ratio and the number of equivalent contact stages used are interadjusted so as to strip and recover 95% or more of the glycerine entering in the feed. Under usual conditions, salt will precipitate in the latter stages of the extraction system and may be settled and withdrawn from the aqueous layer at one or more convenient points. The concentration of the solvent layer will vary according to the composition of the incoming feed, the solvent ratio used, the temperature, and the reflux. Although not an essential requirement, the solvent layer leaving this portion of the extraction system may be passed countercurrent to a small portion of the aqueous glycerine extract from which solvent has been removed and which may have been partially concentrated relative to water or not as desired. The quantity of this reflux is so adjusted in relation to its composition and that of the solvent layer that complete miscibility of the two does not ensue. The use of this reflux increases the concentration of glycerine and decreases the concentration of salts dissolved in the alcohol extract appreciably beyond that which can be obtained without its use.

The small quantity of solvent dissolved in the aqueous residue layer may be recovered and separated from water by evaporation and fractionation. However, it is preferred to recover it as shown in the flow sheet by extraction of the residue with a secondary solvent, such as a hydrocarbon solvent of the type of solvent naphtha boiling considerably above the alcohol and to separate the alcohol and hydrocarbon by fractional distillation of the alcohol, returning both to the system eventually.

Example 2

As illustrated in Figure 25, relatively dilute (10%) aqueous glycerine (low salt content) is countercurrently (preferably continuously) extracted with a primary glycerine selective solvent, such as aniline, benzyl alcohol, or cyclohexanol at a temperature between 20° and 80° C., to yield an extract containing, for example, 15 to 35% glycerine content varying with the particular solvent, temperature, and composition of the feed. The primary solvent is recovered by secondary extraction with a hydrocarbon solvent giving a solvent-free extracted glycerine. By employing reflux, this solvent-free extracted glycerine of about 60 to 80% glycerine content is obtained. The aqueous glycerine concentrated from the dilute feed extraction, 60 to 80% glycerine, or a mixture of similar concentration derived directly from some other source is further concentrated and the glycerine recovered by extraction with a glycerine selective solvent such as saturated tert-amyl alcohol. A solvent-free extracted glycerine of concentration of 90 to 97%, depending on solvent and conditions, is obtained.

Further processes which have been devised for extracting and concentrating glycerine with solvents are briefly as follows: They are found most advantageous to apply to dilute impure aqueous glycerines containing dissolved ionized substances such as salt. Conduct of the several steps is

analogous to that described under Example 1 above.

Example 3

As illustrated in Figure 26, a relatively dilute alkaline aqueous glycerine is extracted at atmospheric temperature with isopropanol by countercurrent extraction substantially to strip the glycerine, remove salt, to purify the extract and to concentrate the glycerine. The extract is freed of solvent which is re-used in a water saturated state. The solvent-free extract slightly acid is countercurrently extracted with dry n-butanol to extract water therefrom. The extract is freed of n-butanol and some water and is returned to the feed of the first or second extraction chamber. The dried n-butanol is re-used. The raffinate is passed to a third stage of extraction wherein it is countercurrently extracted with wet tertiary amyl alcohol at about 50° C. The extract is freed of tertiary amyl alcohol which is re-used. The raffinate is returned to the feed of the first stage of extraction. The extract free of solvent is then countercurrently extracted with glycerine saturated acetone which removes substantially all the water leaving a relatively pure glycerine. The acetone is removed from the extract and re-used. The solvent-free extract goes back to the second or third stage of extraction. The process may be used to employ one stage of aniline extraction in place of the n-butanol and tertiary amyl alcohol or to employ a simple concentration step therefor.

Example 4

As illustrated in Figure 27, a salt-containing aqueous glycerine (slightly basic) is countercurrently extracted with a water-saturated water-selective solvent such at tert-amyl alcohol at a low temperature, or methyl ethyl ketone to strip the glycerine from the feed. The extract is then countercurrently extracted with water to recover the glycerine from the primary solvent. The latter is re-used for extracting fresh feed without necessity for distillation except to remove accumulated impurities. The weak glycerine largely free from salt and purified is extracted with a water immiscible, glycerine selective solvent such as aniline to concentrate, recover and more highly purify the glycerine. This method has the advantage of employing a good selective solvent more effectively than it can be used directly on a feed containing a high percentage of salt. It also effects a high degree of salt removal and purification.

Example 5

Referring to Figure 28, the crude feed, e. g., a soap lye containing about 10% glycerine and about 15% of inorganic salts in solution is extracted in a continuous countercurrent extractor at room temperature with isopropanol. The ratio of solvent to feed is adjusted so as to strip between 90% and 95% of the glycerine from the feed. The extract phase is then led to the solvent recovery apparatus where the solvent is removed. This solvent recovery apparatus is indicated generally and may be a still or a second countercurrent extractor or other apparatus depending upon which of the solvent recovery methods discussed below is used. The isopropanol is preferably recovered wet, with a certain portion of water. This wet isopropanol is re-used in the first extractor, and thus assists in preferentially stripping the glycerine from the incoming feed. It is necessary to add some fresh isopropanol to the solvent feed, inasmuch as some isopropanol is carried back with the raffinate from the extractor, and some isopropanol is carried forward with the concentrated glycerine solution to the second extractor. If desired, the isopropanol in the raffinate may be recovered.

The glycerine solution, largely freed from inorganic salt impurities and containing a small amount of isopropanol is then extracted in the second continuous countercurrent extractor with aniline, in the same manner as the extraction was carried out in the first stage. An extraction temperature of about 25° C. is used. The extract phase is treated in the same manner to recover the aniline therefrom, which is re-used in the extraction. The aniline may be re-used wet, and a certain amount of aniline is added continuously as make-up.

Since a fairly concentrated glycerine solution is being processed in the second extractor, the raffinate phase therefrom will contain normally a considerable precentage of glycerine, unless very large amounts of aniline are used to substantially completely strip the glycerine, and the extraction apparatus provides an extremely long path for countercurrent flow. To recover this glycerine, the raffinate is extracted in a third continuous countercurrent extractor with a water-selective solvent, methyl ethyl ketone at room temperature, or about 25° C. The methyl ethyl ketone strips water from the incoming glycerine solution. The quantity of solvent feed is adjusted to strip sufficient water from the glycerine feed to bring its concentration approximately to the concentration of the glycerine feed of the second extractor. The glycerine solution in the raffinate is fed back into the aniline extractor and thus reprocessed. The methyl ethyl ketone solvent is treated in a solvent recovery apparatus and re-used in the third extractor. The water separated from the methyl ethyl ketone is discarded. The methyl ethyl ketone soon becomes saturated with glycerine, and removes no more from the cycle, except that necessary to saturate the small amount of make-up necessary. The amount of make-up necessary is very small, since that lost in the raffinate from the third extractor is mainly returned to the process with the raffinate from the second extractor, while the solvent recovery apparatus is operated to secure a nearly complete separation of water and methyl ethyl ketone.

The extract phase from the second extractor, after the removal of the aniline, is then extracted in a continuous countercurrent manner with water-saturated tertiary amyl alcohol. The glycerine solution being fed to this extractor is already quite concentrated and the extract from this fourth extractor will have a glycerine content of from 90 to 95% on a solvent-free basis depending upon the quantity of solvent used and the conditions. The solvent is recovered from the extract layer in the manner described in connection with the preceding extraction steps. The raffinate from this fourth extractor will also contain a considerable amount of glycerine. As shown, this raffinate is returned to the feed of the second extractor for reprocessing. By changing the operating conditions, the amount of glycerine stripped from the feed to this fourth extractor may be varied, making it preferable to return this raffinate to the original feed, or making the use of another extraction step to strip water

from this raffinate to concentrate it before it is reprocessed preferable.

In the foregoing examples and particularly in the Figures 24 through 28, inclusive, illustrating the examples, the processes have been illustrated in a diagrammatic manner. In Figures 24 and 25 the method of recovering the primary solvent from the phase has been illustrated as being by the use of a secondary solvent and a countercurrent solvent extraction therewith. In Figures 26, 27 and 28 the solvent separator has been illustrated generically to indicate that any method such as distillation, a secondary solvent extraction or any of the methods discussed below and suitable for the extraction of particular solvent used as the extraction medium may be used. The solvent being carried off with the raffinate, although generally small in amount, may justify recovery. Such recovery has not been shown in the figures or described in the examples but from an economical standpoint might be installed. In describing the examples, it has been assumed that the solvent is completely extracted from the concentrated glycerine solution before this solution is sent to the next stage of the extraction process. In commercial operation, it would generally prove uneconomical to extract completely the solvent from the extract phase. Small amounts of solvent will therefore be present with the aqueous glycerine solution being treated in all but the first stage of a multi-stage extraction process. Where the process is operated with three or more stages a solvent mixture may be present in the aqueous glycerine solution being treated. The amounts of the solvents in the aqueous glycerine solution are preferably small, however, and do not materially affect the operation of the process. The effect is substantially the same as that described above in connection with the use of solvent mixtures except that the mixture is not generally intentional and that one component of the solvent mixture is by far the major component while the other component or components are substantially to be considered as impurities. Where the two solvents are both either glycerine-selective or water-selective and have generally similar properties in other respects, the small amount of impurity merely operates as though a little more of the primary solvent were being used. Where one is water-selective and the other glycerine-selective, under the conditions in the extractor, the impurity obviously detracts somewhat from the desired effect of the principal solvent and should not be allowed to reach too high a value.

In accomplishing the separation of water and glycerine and extracting and concentrating glycerine with solvents, for the sake of economy, it is desirable to remove not only the solvent from the more concentrated glycerine-solvent extract layer but also the small quantity of solvent dissolved in the aqueous residue layer, and to recover the solvent for re-use. The residue layer containing water, impurities and dissolved salts is discarded from the extraction system after its solvent has been receovered. It is proposed to accomplish the removal and recovery of solvent either by evaporation or distillation at atmospheric or sub-atmospheric pressure, or by a secondary extraction of the primary solvent from the primary extract and residue layers with a suitable secondary solvent. The latter dissolves the primary solvent preferentially, and preferably is almost completely immiscible with both water and glycerine and has a boiling point differing considerably from that of the primary solvent.

In removing the solvent directly by vaporization methods, the evaporation or distillation is conducted either so as to remove substantially only the water content or only the solvent content of the extract; or, in other cases, one may remove both together from the extract. If the solvent is more volatile from the extract layer and raffinate layer than water, one may first evaporate off the solvent together with the water which accompanies it and fractionally distill to separate water and solvent in a separate step; or one may fractionally distill so as to remove the solvent and simultaneously separate it from water in the same step. In either case, glycerine containing more or less water is the residue. If the solvent is less volatile than water, the latter is simultaneously removed overhead in vaporizing the solvent to remove it. Whether or not fractionation is necessary and the extent to which it need be carried is determined by the miscibility of water and the solvent. If these are immiscible, they may be largely separated by simple condensation and decantation.

As an example, in removing the solvent from tertamyl alcohol extracts by evaporation under reduced pressure, it has been ascertained that water vaporizes off at low temperature as a constant boiling mixture with the alcohol and is largely removed with the first portions of the solvent in the first stages of the evaporation, leaving behind a solution of very strong glycerine in alcohol. Evaporation may be continued to remove the residual alcohol or it may then be removed by the method of secondary extraction. The constant boiling mixture of water and alcohol separates into two layers on condensation and the two may be separated by decantation; complete separation of the water from the alcohol is ordinarily unnecessary as the wet solvent may be re-used in the extraction. As another illustration, when the isopropyl alcohol is removed by evaporation from an isopropyl alcohol extract from a soap lye, this solvent being more volatile than water comes off first together with some water. When the alcohol is off, the residual glycerine is concentrated to 50 to 60%. Suitable fractionation separates water from the alcohol giving overhead a recovered alcohol sufficiently dry for re-use. This process might have been continued to remove as much of the water as desired from the glycerine along with the alcohol. Fractionation of the alcohol and water may be effected simultaneously with the removal of the solvent or in a separate step.

For many reasons it has been found advantageous to remove and recover the solvent from extracts and residues in the solvent extraction of glycerine by extracting the primary solvent therefrom by a secondary extraction with a second solvent specifically selected for this purpose. This is particularly the case if the primary solvent is appreciably less volatile than water and/or if it is present in small amounts as is the case in the aqueous residues. The vaporization of a large quantity of water is thus avoided which is especially advantageous in recovering solvent from the aqueous residues (in this connection, it should be remembered that the latent heat of vaporization of water is 3 to 6 times that of organic solvents employed). Further, it is thus possible to avoid heating the glycerine above normal temperatures. In such cases, if desired, the extract may be heated to remove the water

as a binary with part of the primary solvent before extracting the remaining primary solvent from the extract with the secondary solvent. The secondary solvent may be so selected as to make its separation and recovery from the primary solvent relatively easy and simple. In using a secondary extraction to remove and recover primary solvent as part of the extraction processes for glycerine, the secondary solvent is brought into contact with the aqueous residue to remove its solvent and then into contact with the extract and subsequently the primary and secondary solvents are separated and recovered for re-use by distillation. While as the secondary solvent, one might employ any solvent dissolving the primary solvent in preference to glycerine or to water and glycerine, it is preferred to use one essentially immiscible with water and glycerine and having a boiling point either considerably higher or lower than the primary solvent. For example, as secondary solvents, one may employ hydrocarbons, such as kerosene, solvent naphtha, or other petroleum fractions, benzene, toluene, xylene; chlorinated and nitrohydrocarbons; high molecular weight ethers and chlorinated ethers, e. g., dibutyl ether, dichlorodi-ethyl ether; and highly water-selective solvents and others. The secondary extraction may be accomplished at the same temperature or at temperatures substantially different from those for optimum operation of the primary extraction.

Other methods for recovering the solvent include the partial recovery of a solvent having a relatively high melting point by freezing the solvent from the extract by cooling it well below its normal melting point. Tertiary butyl alcohol which has a melting point in the normal atmospheric range is particularly suitable for this purpose. Another method is to employ highly reactive solvents, such as aniline or other amines, and to remove them from the extract by converting them to their salt by reaction with suitable acids such as hydrochloric or sulphuric acid and crystallizing the salts from the extract with or without cooling. A still further recovery system is to take advantage of the change in solubilities with changes in temperatures. For example, it is possible to extract selectively water from aqueous glycerol by means of tertiary amyl alcohol at relatively low temperature, e. g., 7.6° C., and then to warm the aqueous layer containing, say about 9% tertiary amyl alcohol to about 25° C., at which temperature about 7% of the mixture separates out as a supernatant layer having a tertiary amyl alcohol content of about 72%, and an even higher glycerine to water ratio. Similar recoveries may be accomplished with the solvent layers and with other solvents such as isopropanol. Likewise, addition of salts or alkali aids in the separation of the solvent. Although, if this procedure be used so that a purification and concentration of glycerine may have been attained, it does have some disadvantages in that the aqueous or glycerine layer is admixed with large quantities of salt.

In dealing with impure aqueous glycerine solutions containing large amounts of dissolved inorganic salts, it is frequently desirable to operate the first stage of a multistage extraction process in such a manner that purification and freedom from the salt impurity is its major object and concentration of glycerine is secondary. In such a case, an extraction procedure is used in the first stage of the process in which the feed of aqueous glycerine is first extracted with a glycerine-selective partially water immiscible solvent, such as saturated tertiary amyl alcohol, isopropanol or methyl ethyl ketone. The extract from such an extraction is free of most water-soluble impurities. This extract is re-extracted with water in order to strip the glycerol from the solvent. The recovered solvent which is then water-saturated as is desirable for the first stage of extraction is then ready for re-use. The aqueous glycerol is substantially free of water-soluble impurities. Such an extraction process is illustrated in Figure 27 and specifically described in connection with the discussion of Example 4. The aqueous glycerine solution freed from salts may then be further concentrated in subsequent stages of the extraction process.

The processes of this invention may be varied by employing addition agents, organic and/or inorganic, to affect the selectivity of and concentration in the solvent. Twitchell reagents, other aromatic sulphonic acid salts, other organic or inorganic acids, bases or salts may be added for this purpose.

The process is also applicable to the securing of other polyhydric alcohols than glycerine, such as mannitol, sorbitol, erythritol, dulcitol, beta methyl glycerine, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol; 1,4 pentandiol; 1,2,5 pentantriol; hexoses, and other sugars and in fact any polyhydroxy organic material.

As many widely different embodiments of the present invention may be made without departing from the spirit or scope thereof, it is not to be limited except as defined in the following claims.

I claim:

1. The process of concentrating aqueous glycerine solutions which comprises contacting a relatively concentrated aqueous glycerine solution with at least one organic solvent which is ordinarily at least partially immiscible with glycerine and which dissolves a substantial quantity of water at the operating temperature in the presence of sufficient glycerine to form at least two liquid phases under the operating conditions, separating the two layers to obtain a more highly concentrated glycerine from the raffinate, subsequently contacting the thus concentrated glycerine solution with at least one different organic solvent which under the operating conditions existing in this second solvent treatment step dissolves a substantial amount of one of the liquid components of the glycerine solution in a higher ratio to the other components than in the solution being treated in this second solvent treatment step, in such proportions and under such conditions that at least two liquid phases are formed, and recovering the glycerine from the phase in which it is in a higher ratio.

2. The process of concentrating aqueous glycerine solutions which comprises contacting an aqueous glycerine solution with at least one organic solvent, which is ordinarily at least partially immiscible with glycerine and which dissolves a substantial quantity of water at the operating temperature, in the presence of sufficient glycerine to form at least two liquid phases under the operating conditions, separating the two phases to obtain a more highly concentrated glycerine from the raffinate, removing any organic solvent from the raffinate, treating the concentrated aqueous glycerine solution obtained by contacting therewith at least one different organic solvent which under the operating conditions dissolves a substantial amount of glycerine in a

higher ratio to water than in the concentrated aqueous glycerine solution being treated in this second solvent treatment step, in such proportions and under such conditions that at least two liquid layers are formed, separating the two layers and recovering the more highly concentrated glycerine from the extract layer.

3. The process of treating glycerine solutions which comprises contacting an aqueous glycerine solution with organic solvents in a plurality of steps using at least one different organic solvent in each step which under the operating conditions existing in said step is partially immiscible with the water and glycerine mixture being treated, but dissolves a substantial portion of one of these components in a higher ratio to the other than in the solution being treated originally in each step, in such proportions and under such conditions that at least two liquid phases are formed and separating the phases formed in each step, using the phase containing the higher ratio of glycerine to water as the material being treated in the next step of the process, and recovering the concentrated glycerine from the phase containing the higher ratio of glycerine to water as the final step of the process.

4. The process of concentrating aqueous glycerine solutions containing inorganic salt impurities which comprises contacting the aqueous glycerine solution with isopropanol in such proportions and under such conditions that two liquid phases are formed, separating the two liquid phases, removing the isopropanol from the extract phase, treating the concentrated glycerine solution remaining after the isopropanol has been substantially removed by subsequently contacting therewith tertiary amyl alcohol in such proportions and under such conditions that two liquid phases are formed and recovering the concentrated glycerine from the extract phase.

5. The process of concentrating aqueous glycerine solutions which comprises contacting the aqueous glycerine solution with aniline in such proportions and under such conditions that two liquid phases are formed, separating the two liquid phases, removing the aniline from the extract phase, treating the concentrated glycerine solution remaining after the aniline has been removed by subsequently contacting therewith methyl ethyl ketone in such proportions and under such conditions that two liquid phases are formed, separating the two phases and recovering the concentrated glycerine from the raffinate phase.

6. The process of concentrating aqueous glycerine solutions containing inorganic salt impurities which comprises contacting the aqueous glycerine solution with tertiary butyl alcohol in such proportions and under such conditions that two liquid phases are formed, separating the two liquid phases, removing the tertiary butyl alcohol from the extract phase, treating the concentrated glycerine solution remaining after the tertiary butyl alcohol has been removed by subsequently contacting therewith tertiary amyl alcohol in such proportions and under such conditions that two liquid phases are formed, separating the two phases and recovering the concentrated glycerine from the extract phase.

7. The process of treating glycerine solutions which comprises contacting an aqueous glycerine solution with organic solvents in a plurality of steps using at least one different organic solvent in each step which under the operating conditions existing in said step is partially immiscible with the water and glycerine mixture being treated, but dissolves a substantial portion of one of these components in a higher ratio to the other than in the solution being treated originally in each step, in such proportions and under such conditions that at least two liquid phases are formed and separating the phases formed in each step, separately contacting the phases with a substantially water immiscible solvent to recover the solvents used in each step from the two phases, using the phase containing the higher ratio of glycerine to water as the material being treated in the next step of the process, and recovering the concentrated glycerine from the phase containing the higher ratio of glycerine to water as the final step of the process.

8. The process of treating glycerine solutions which comprises contacting an aqueous glycerine solution with organic solvents in a plurality of steps using at least one different organic solvent in each step which under the operating conditions existing in said step is partially immiscible with the water and glycerine mixture being treated, but dissolves a substantial portion of one of these components in a higher ratio to the other than in the solution being treated originally in each step, in such proportions and under such conditions that at least two liquid phases are formed and separating the phases formed in each step into a raffinate phase and an extract phase, countercurrently extracting first the raffinate phase and then the extract phase with a substantially water immiscible solvent to recover the solvents used in each step from the two phases, using the phase containing the higher ratio of glycerine to water as the material being treated in the next step of the process, and recovering the concentrated glycerine from the phase containing the higher ratio of glycerine to water as the final step of the process.

9. The process of concentrating aqueous glycerine solutions which comprises contacting an aqueous glycerine solution with at least one organic solvent which is at least partially immiscible with water and which dissolves a substantial quantity of glycerine at the operating temperature in the presence of sufficient water to form at least two liquid layers under the operating conditions, separating the two layers to obtain a more highly concentrated aqueous glycerine solution from the extract layer, substantially removing the solvent from the extract layer, and subsequently contacting the thus concentrated glycerine solution with at least one different organic solvent which under the operating conditions existing in this second solvent treatment step dissolves a substantial amount of one of the liquid components of the glycerine solution in a higher ratio to the other components than in the solution being treated in this second solvent treatment step, in such proportions and under such conditions that at least two liquid phases are formed, and recovering the glycerine from the phase in which it is in a higher ratio.

10. The process of concentrating aqueous glycerine solutions containing considerable amounts of inorganic salt impurities which comprises contacting the glycerine solution with an organic solvent which is at least partially immiscible with the aqueous salt solution and which dissolves a substantial quantity of glycerine at the operating temperature in the presence of sufficient aqueous salt solution to form at least two liquid layers under the operating conditions, separating the two liquid layers into an extract layer and a

raffinate layer, the raffinate layer containing the major portion of the inorganic salts, substantially removing the solvent from the extract layer, and subsequently contacting the thus concentrated and purified glycerine solution with at least one different organic solvent which under the operating conditions existing in this second solvent treatment step dissolves a substantial amount of one of the liquid components of the glycerine solution in a higher ratio to the other components than in the solution being treated in this second solvent treatment step, in such proportions and under such conditions that at least two liquid phases are formed, and recovering the glycerine from the phase in which it is in a higher ratio.

11. In a process of treating aqueous glycerine solutions which comprises contacting the aqueous glycerine solution with organic solvents in a plurality of steps using at least one different organic solvent in each step which under the operating conditions existing in said step is partially immiscible with the water and glycerine mixture being treated therein, but dissolves a substantial portion of one of these components in a higher ratio to the other than in the solution being treated originally in each step, in such proportions and under such conditions that at least two liquid phases are formed and separating the phases formed in each step, using the phase containing the higher ratio of glycerine to water as the material being treated in the next step of the process, and recovering the concentrated glycerine from the phase containing the higher ratio of glycerine to water, the step which comprises using as the solvent in the final stage of the process an organic solvent which dissolves glycerine in a lower ratio to water than exists in the aqueous glycerine solution being treated in this final step under the conditions existing in this extraction step, and substantially saturating the solvent with glycerine, whereby the solvent substantially removes the remaining water, only, from the glycerine solution.

12. In a process of treating aqueous glycerine solutions which comprises contacting the aqueous glycerine solution with organic solvents in a plurality of steps using at least one different organic solvent in each step which under the operating conditions existing in said step is partially immiscible with the water and glycerine mixture being treated therein, but dissolves a substantial portion of one of these components in a higher ratio to the other than in the solution being treated originally in each step, in such proportions and under such conditions that at least two liquid layers are formed and separating the layers into an extract layer and a raffinate layer, using the phase containing the higher ratio of glycerine to water as the material being treated in the next step of the process, the step which comprises using as a solvent in at least one step of the process a solvent which dissolves glycerine to water in a higher ratio than in the solution being treated in that step giving a concentration of the aqueous glycerine in the extract layer, recovering the glycerine in the raffinate layer by contacting therewith a glycerine saturated solvent in such proportions and under such conditions that two layers are formed, an extract layer and a raffinate layer, separating the layers, and returning the thus concentrated glycerine solution in this latter raffinate layer back to process for recycling.

13. The process of claim 12, in which the concentrated glycerine solution in the raffinate is returned to the process as a portion of the aqueous glycerine feed to the step in which the glycerine selective solvent is being used, for recycling directly in that step.

14. The process of claim 12, in which the glycerine saturated solvent is methyl ethyl ketone.

15. The process of concentrating aqueous glycerine solutions containing inorganic salt impurities which comprises contacting the aqueous glycerine solution with isopropanol in such proportions and under such conditions that two liquid phases are formed, separating the two liquid phases into an extract phase and a raffinate phase, treating the concentrated glycerine solution in the extract phase remaining after the isopropanol has been substantially removed by subsequently contacting therewith aniline in such proportions and under such conditions that two liquid phases are formed, separating the two liquid phases into an extract phase and a raffinate phase, contacting the raffinate phase from the aniline extraction step with methyl ethyl ketone substantially saturated with glycerine in such proportions and under such conditions that two liquid phases are formed, separating the two phases into an extract phase and a raffinate phase, returning the raffinate phase from the methyl-ethyl ketone extraction step back into the aqueous glycerine solution before contacting with the aniline, and recovering the glycerine from the extract phase from the aniline extraction step.

16. The process of claim 15 in which the glycerine solution in the raffinate from the aniline extraction step is contacted with a proportion of the glycerine saturated methyl ethyl ketone sufficient to extract an amount of water to make the concentration of the aqueous glycerine being discharged from the methyl ethyl ketone extractor in the raffinate substantially equal to the concentration of the aqueous glycerine being extracted with aniline.

17. In a process of treating aqueous glycerine solutions which comprises countercurrently contacting the aqueous glycerine solution with organic solvents in a plurality of steps using at least one different organic solvent in each step which under the operating conditions existing in said step is partially immiscible with the water and glycerine mixture being treated therein but dissolves a substantial portion of one of these components in a higher ratio to the other than in the solution being treated originally in each step, in such proportions and under such conditions that at least two liquid phases are formed and separating the phases into an extract phase and a raffinate phase, using the phase containing the higher ratio of glycerine to water as the material being treated in the next step of the process, the step which comprises substantially removing the solvent from the extract phase of one of the steps of the process, returning a portion of the solvent-free extract to the countercurrent extraction step from whence it came and flowing this solvent-free extract countercurrent to the solvent-extract phase, feeding the aqueous glycerine solution being processed at an intermediate point in the extraction step and flowing this solution countercurrent to the solvent-extract flow, whereby the concentration of the constituent being selectively dissolved by the solvent phase is increased beyond that in equilibrium with the aqueous glycerine solution feed.

18. In a process of treating aqueous glycerine

solutions containing dissolved inorganic salt impurities which comprises countercurrently contacting the impure aqueous glycerine solution in a plurality of steps using at least one different organic solvent in each step which under the operating conditions existing in said step is partially immiscible with the water and glycerine mixture being treated therein, but dissolves a substantial portion of one of these components in a higher ratio to the other than in the solution being treated originally in each step, in such proportions and under such conditions that at least two liquid phases are formed and separating the phases into an extract phase and a raffinate phase, using the phase containing the higher ratio of glycerine to water as the material being treated in the next step of the process, the step which comprises using a glycerine selective solvent in at least one step of the process giving a concentration of aqueous glycerine in the extract phase, removing the solvent from the extract, returning a portion of the thus concentrated glycerine solution to the countercurrent extraction step from whence it came and flowing the glycerine solution countercurrent to the solvent-extract phase, whereby the salt content of the solvent-extract phase is reduced below that in equilibrium with the aqueous glycerine solution feed, and feeding the aqueous glycerine solution containing the inorganic salt impurities at an intermediate point in the extraction step and flowing this solution countercurrent to the solvent-extract flow.

19. The process of claim 18, in which the aqueous glycerine solution containing inorganic salt impurities being fed at an intermediate point in a solvent extraction step is admitted at a point at which the salt content of the impure glycerine solution is the same as that of the glycerine solution from the extract phase being extracted by the solvent.

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