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PROCESS OF REFINING GLYCERIN

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This invention relates in general to the purification of essentially anhydrous glycerine, and more particularly to a process for refining essentially anhydrous glycerine obtained by the transesterification of fatty materials.

From time immemorial, glycerine has been obtained chiefly as a by-product of the soap making industry. Conventional soap making processes involve the saponification of suitable fatty materials with an alkali such as sodium or potassium hydroxide. The reaction produces the alkali metal soaps of the fatty acids and glycerine. In the process of separating the soap from the reaction mass and purifying it, considerable quantities of water and common salt are utilized in the form of brine. Thus the glycerine resulting from the saponification process ends up in a very dilute aqueous solution, which solution contains not only the glycerine but also considerable salt as well as various impurities originally associated with the fatty material or resulting from side reactions during the saponification. In order to obtain a relatively pure, high quality glycerine from this impure, dilute aqueous solution, or spent soap-lye as it is commonly known, numerous involved processes have been proposed. Such processes not only add to the cost of the final product, but also it is relatively difficult to obtain good yields of anhydrous glycerine thereby. A part of this poor recovery of the glycerine is inherent in the saponification process itself; however, a considerable amount of the loss is directly attributable to the inefficiency of the recovery processes.

In recent years it has been proposed to prepare esters of the fatty acids by reacting fatty materials with low molecular weight, monohydric alcohols such as methanol or ethanol in the presence of alkaline or acidic transesterification catalysts. These esters, after separation from the reaction mass and purification, may be used per se or saponified to produce high quality soaps. The glycerine which results from such transesterification of glycerides is in an essentially anhydrous condition; however, the glycerine does have associated with it various impurities which were originally associated with the fatty material, were produced by side reactions during the transesterification process, or were added to or produced in the reaction mixture incident to the separation and purification of the end products. Difficulties have been encountered in removing these impurities from the crude essentially anhydrous glycerine and obtaining purified, high quality glycerine. In one transesterification process, it

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is recommended that the glycerine obtained be diluted with water before an attempt is made to purify it. Not only does this discard the advantage of having obtained the glycerine in an anhydrous state, but also the addition of the water increases the solubility of certain of the impurities in the resulting glycerine solution thus increasing the difficulty of refining the glycerine as regards these impurities.

In the copending application of Sprules and Price, Serial No. 761,160, filed July 15, 1947, there is disclosed an improved process for preparing alkyl esters of the fatty acids involving first transesterifying fatty glyceride materials having acid values of at least one with low molecular weight alcohols employing an alkaline material in sufficient quantity to neutralize the free fatty acids in the fatty material, and provide sufficient alkaline material to serve as an alkaline catalyst, and then adding sulfuric or phosphoric acid to the reaction mixture in sufficient amount to split what soaps were previously formed, neutralize the alkaline catalyst, and provide sufficient acidic material to serve as an acid catalyst, and thereafter esterifying the free fatty acids in the mass with the alcohol therein.

It is the object of this invention to provide an improved process for refining the crude, essentially anhydrous glycerine obtained by the Sprules and Price process disclosed in the above-identified application.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has now been discovered that the foregoing and other objects of the invention may be realized by reacting the acid catalyst after the esterification of the free fatty acids is completed, either with or without separating the acidic, crude anhydrous glycerine from the reaction mass, with an alkaline earth oxide or hydroxide, i. e. an oxide or hydroxide of calcium, barium, or strontium, subsequently treating the crude anhydrous glycerine with a small amount of an ammonium halide by admixing such a compound therewith, heating the mixture for a short time and then removing any insoluble materials from the glycerine to recover an excellent quality, anhydrous, refined glycerine. This refined and essentially anhydrous glycerine may be further purified, if desired, by distillation, codistillation with mineral oil, or by solvent extraction, or by a combination of such further refining processes.

The manner in which our refining process brings about the desired transformation of the crude anhydrous glycerine to the ultimate re-

fined product has not been definitely determined, but one possible explanation is as follows: Using the oxides MO, where M is barium, strontium or calcium, and assuming for purposes of illustration that some form of sodium has been employed as the alkaline catalyst and that sulfuric acid has been employed as the acid catalyst, the sulfate in the crude glycerine is converted into insoluble alkaline earth sulfate and an equimolar amount of sodium hydroxide is also formed according to the following equation:

$$MO + NaHSO_4 \longrightarrow \underline{MSO_4} + NaOH$$

Any very small excess of sulfuric acid is converted to the alkaline earth sulfate according to the following equation:

$$MO + H_2SO_4 \longrightarrow \underline{MSO_4} + H_2O$$

If the hydroxide is used, the following equations corresponding to the above apply:

$$M(OH)_2 + NaHSO_4 \longrightarrow \underline{MSO_4} + NaOH + H_2O$$

$$M(OH)_2 + H_2SO_4 \longrightarrow \underline{MSO_4} + 2H_2O$$

In the last pair of equations much more water is formed by the neutralization steps and for this reason the use of the oxide is preferred.

In the second step of the refining process the ammonium halide (NH_4X) neutralizes the sodium hydroxide which has been formed during the first step of the process, and ammonia is liberated according to the following equation:

$$NaOH + NH_4X \longrightarrow \underline{NaX} + H_2O\ \overline{NH_3}$$

In this manner, the residual acidic salts in the crude glycerine are all converted to neutral salts which are insoluble in the glycerine and can be removed by filtration.

The explanation of the manner in which the process may work applies equally as well if the acid catalyst is phosphoric acid instead of sulfuric acid or if an alkali metal compound other than a sodium compound is employed as the alkaline catalyst. The suggested mechanism for the process is well borne out in practice, but we do not limit ourselves to such an explanation.

Regardless of whether the above explanation is the proper one, we do know that the refining process as set forth above, i. e. reaction of the acid catalyst with one of the basic compounds listed, followed by treatment of the crude essentially anhydrous glycerine with a halide salt as set forth and subsequent removal of insoluble materials from the glycerine-salt mixture, will produce an excellent grade of refined essentially anhydrous glycerine much more simply and with greater yields than previous refining processes. In view of the difficulties which have been encountered in the prior art in attempting to refine the glycerine obtained by transesterification processes, it is very likely that during our refining process various chemical reactions take place in addition to the ones which we have outlined. Furthermore, the inorganic salts which we employ in our refining process undoubtedly exert various physical effects which aid in converting the various impurities in the glycerine into a form in which they may readily be separated from the glycerine. Thus it is quite apparent that the mechanism of our process is considerably more involved than the simplified explanation given above might indicate.

In the Sprules and Price process of producing the alkyl esters from the fatty materials through transesterification followed by esterification, some water is unavoidably produced whenever the alkaline catalyst which is employed is one of the alkali metal hydroxides. The water is formed when the hydroxide is neutralized with either sulfuric or phosphoric acid preparatory to carrying out the esterification step of that process; however, since the amount of alkaline catalyst which is employed is quite small only a very small amount of water is produced by such neutralization. A small amount of water is also produced by the chemical reactions involved in our refining process, but the amount produced in that manner is also quite small. In fact the total amount of water produced by both the neutralization of the alkaline catalyst when such catalyst is an alkali metal hydroxide and by the reactions which occur in our refining process is so small that, comparatively speaking as regards such sources of water, the glycerine produced will be relatively water-free.

If the fatty material being employed in the Sprules and Price process has a relatively low acid value, e. g. 10 or below, the amount of water produced by neutralization of the free fatty acids prior to carrying out the transesterification step of that process will be quite small. However, when the fatty material has a relatively high acid value, the amount of water produced by the neutralization of the free fatty acids will be appreciable. Therefore, in order to obtain relatively anhydrous glycerine in such a case, it is preferred to carry out the Sprules and Price process under conditions such that the water of reaction will be continuously removed, e. g. by carrying out the process under reflux conditions and continuously separating the water from the alcohol being employed either by drying the alcohol-water azeotrope over caustic alkali, or by mechanically separating the water from the alcohol in a Dean trap when the alcohol employed is one relatively immiscible with water, or by any other suitable means. However, if desired, the Sprules and Price process may in all cases be carried out under conditions such that the water of reaction will be continuously removed.

Any water left in the glycerine after the main steps of our refining process will be removed for the most part when the glycerine is freed of any of the alcohol used in producing the alkyl esters which is still associated with the glycerine. Also if the refined glycerine is itself distilled under reduced pressure so as to obtain a completely pure product, it may be completely freed during such distillation of any water still associated therewith, and thus refined, completely anhydrous glycerine may be obtained.

In carrying out the process of the invention, the crude essentially anhydrous acidic glycerine is first treated with a basic compound selected from the group consisting of calcium hydroxide, barium hydroxide, strontium hydroxide, calcium oxide, barium oxide and strontium oxide. This treatment may be carried out on the entire reaction mass prior to the removal of the essentially anhydrous glycerine therefrom, but preferably the glycerine is first removed and then treated. After the essentially anhydrous glycerine has been so treated, either as a part of the esterification reaction mixture or after separation from the reaction mixture, it may be filtered, if desired, to remove any insoluble material therein. If desired, the treated glycerine may be heated for a short time prior to such filtration since such heating will often aid in converting the insoluble impurities therein into a form more readily removable

by filtration. Such heating may conveniently be carried out by heating the treated glycerine at about 60° C. or above by any convenient means, e. g. by a steam bath, for a short time, e. g. about half an hour.

The glycerine is then further treated by admixing therewith a small amount of one of the halide compounds suitable for use in the second step of the refining process. If the first treatment with the metal oxides or hydroxides is carried out without separating the essentially anhydrous glycerine from the esterification reaction mass, such a separation is made before adding the halide compound to the glycerine. In order to have a relatively fluid material to work with, it is usually preferred to allow a small amount of the alcohol employed in the esterification to remain with the glycerine during the refining. Not only does it give a material which is easier to handle, but it also helps to prevent loss of glycerine due to adherence to filters during filtration. If, for some reason or other, all of the alcohol has been separated from the essentially anhydrous glycerine during the removal thereof from the esterification mixture, a suitable amount of the esterification alcohol or a similar alcohol may, if desired, be added to the glycerine so that it will be less viscous. However, this is not necessary and, if it is preferred, the process may be carried out on essentially anhydrous glycerine completely free of alcohol. After admixture of the anhydrous glycerine and the halide compound, the mass is heated for a short time. The heating may be carried out at any desired temperature below that which would deleteriously affect the glycerine. A suitable temperature is from about 60° C. to about 120° C. When the glycerine being treated still has alcohol associated therewith, the heating may suitably be carried out in general at the reflux temperature of the alcohol. The length of time of heating may vary considerably; however, heating for about half an hour to an hour will in most cases bring about the desired degree of refining although the mass may be heated for a longer period, if desired. After the treatment with the halide compound the glycerine is filtered to remove any insoluble salts and any other insoluble matter. The product obtained is a light colored, essentially anhydrous glycerine of good quality. If any alcohol is still admixed with the glycerine, it may readily be removed by a simple distillation.

The essentially anhydrous glycerine obtained by the process as described hereinabove is of good quality, and for many purposes for which it may be used, e. g. as a plasticizer, in adhesives, etc., no further treatment whatsoever is necessary; however, for some purposes it may be desirable to refine the glycerine further. Occasionally the glycerine will have a rather opaque or cloudy appearance or in some cases it may even be viscous or pasty. This is caused by the presence in the glycerine of small amounts of salts and other impurities which in some cases may be of such small particle size that it will sometimes be difficult, if not impossible, to remove them by ordinary filtration. If it is desired to further refine the essentially anhydrous glycerine by distillation thereof under reduced pressure, it is rather important to remove relatively large percentages of such impurities present prior to the distillation since we have found that their presence during the distillation may tend to decompose the glycerine thus reducing the final yield and deleteriously affecting the quality of the product as some of the decomposition products distill over with the glycerine giving it undesirable odors and colors as well as reducing the purity thereof.

If any difficulty is encountered in removing such impurities from the glycerine by filtration means, the impurities may be removed for the most part by contacting the essentially anhydrous glycerine containing the impurities with a solvent selected from the group consisting of methanol, ethanol, propanol, butanol, and acetone. The extraction process should preferably be carried out at about room temperature or a temperature below room temperature, and in each extraction the ratio of the solvent to the essentially anhydrous glycerine containing the impurities should preferably be from about 1 to 3 to about 1 to 7 in order to obtain the best results. Under such conditions these solvents, which are immiscible with the impurities in the glycerine, will be found to be somewhat immiscible with the essentially anhydrous glycerine containing the impurities but relatively miscible with glycerine which is more or less free of such impurities. Thus when such a process is carried out, the solvent will extract relatively pure, essentially anhydrous glycerine from the mixture of essentially anhydrous glycerine and impurities. By carrying out successive extractions, the essentially anhydrous glycerine may easily be separated from the greater part of the impurities contained therein. When using acetone as the extracting solvent, it will usually be necessary to carry out a greater number of extractions than when employing the other solvents since acetone is not too miscible with glycerine. The essentially anhydrous glycerine containing the impurities may be contacted with the solvent in any desired manner. A liquid-liquid extraction apparatus may be employed, or if desired a batch extraction process may be used with successive portions of the solvent being contacted with the glycerine. By simply filtering the combined solvent extracts and removing the solvent therefrom, e. g. by distillation under reduced pressure, a fairly pure grade of glycerine will be recovered. This essentially anhydrous glycerine may then, if desired, be readily distilled without any decomposition to give in most cases a colorless, odorless, neutral, anhydrous glycerine of substantially C. P. quality.

If any difficulty is experienced in separating the essentially anhydrous glycerine from the more or less colloidally sized impurities by means of the solvent extraction process as set forth in the previous paragraph, an alternate procedure may be employed. The essentially anhydrous glycerine mass may be completely dissolved in either methanol, ethanol, propanol, or butanol by employing an excess of the solvent. Acetone is then added to the solvent solution until a precipitate of the impurities just begins to form. Preferably an amount of the solvent just sufficient to cause the precipitate to redissolve is then added. The mass is then digested by heating for a short time, e. g. by heating on a steam bath for about half an hour at a temperature of about 50° to 60° C. or above. This treatment will cause practically all of the impurities which are still associated with the essentially anhydrous glycerine to precipitate out, and they may then be readily removed from the glycerine by filtration. After removal of the solvent from the solvent solution of the glycerine, the glycerine may be further purified by distilling it under reduced pressure if desired.

In carrying out the distillation of the essen-

tially anhydrous glycerine under reduced pressure, the glycerine may be co-distilled with mineral oil if desired. Such a procedure will help prevent slight decomposition of the glycerine, and in some cases will help obtain a more nearly complete recovery of the refined glycerine. Any good grade of mineral oil having a boiling point temperature about the same or slightly higher than that of glycerine may be utilized in such a co-distillation process.

Halide salts which are particularly suitable for use in the process of our invention are ammonium chloride, ammonium fluoride and ammonium bromide. Suitable mixtures of these salts may also be used if desired. Of these salts we prefer to employ ammonium chloride in view of the lower cost and ready availability of this compound.

The amount of ammonium halide which is employed in the halide salt treatment step of the invention is preferably determined by calculating the amount thereof which would be required to react with all of the sodium hydroxide, or other similar alkaline compound, present in the glycerine layer. We have found that such an amount of the ammonium halide gives very effective results in refining the essentially anhydrous glycerine.

After treating the reaction mass with either an alkaline earth hydroxide or oxide, and also after the halide treatment step of our process, insoluble materials may be separated from the glycerine by means other than filtration, for example by centrifugation, etc., if desired, as well as by the solvent extraction processes described hereinabove.

For a fuller understanding of the nature and objects of the invention, reference may be had to the following examples which are given merely to further illustrate the invention and are not to be construed in a limiting sense.

Example I

900 parts of peanut oil having an acid value of one were reacted with methanol in the ratio of 15 moles of methanol to 1 mole of gylceride, employing 1% of sodium hydroxide (based on the weight of the glyceride) as an alkaline catalyst. The mixture was refluxed for one hour, cooled somewhat, made acid with 20.2 parts of concentrated sulfuric acid and refluxed for an additional four hours. The reaction mixture was allowed to layer, and the lower glycerine layer was then drawn off. To the glycerine layer there were then added 38 parts of barium oxide and the mixture was heated for one hour on a steam bath. The mixture was cooled and 29.5 parts of ammonium chloride were then added to it, and the mixture then heated for an hour on the steam bath. Most of the methanol associated with the glycerine was then removed by distillation and the reaction mass filtered. The crude glycerine obtained was freed of methanol giving a somewhat viscous, cloudy product. Upon distillation of the crude glycerine under reduced pressure, an odorless, water-white, anhydrous glycerine having a pH of 7 was obtained in a yield of 83.7%.

Example II

900 parts of peanut oil having an acid value of one were treated similarly as in Example I. In treating the glycerine layer, however, the barium oxide was replaced with 18.4 parts of calcium hydroxide. Also only 26.8 parts of ammonium chloride were used. During the filtration of the crude glycerine following the ammonium chloride treatment, a small amount of methanol was added to the glycerine to reduce its viscosity so that it could be filtered more easily. Upon removal of all the methanol from the filtered glycerine, a cloudy, light amber colored product was obtained. Upon distillation of the glycerine at reduced pressure, an 85.5% yield of refined, anhydrous glycerine was obtained.

Example III

904 parts, i. e. one mole, of peanut oil having an acid value of approximately one were transesterified by refluxing for one hour with 480 parts, i. e. 15 moles, of methanol, employing 9 parts of sodium as an alkaline catalyst. 45.2 parts of sulfuric acid were then added and esterification carried out by refluxing for 4 hours. After completion of the esterification reaction, 38.0 parts of calcium hydroxide were added to the reaction mixture. The reaction mixture was then filtered, the excess alcohol removed, and the glycerine separated from the esters. The crude glycerine was then heated with 15 parts of ammonium chloride at about 65° C. for approximately one hour. Any alcohol still associated with the glycerine was then removed by distillation, the glycerine filtered and then vacuum distilled at 2 mm. Excellent quality anhydrous glycerine in an amount equivalent to 81% of the theoretical yield was obtained.

Example IV

880 parts, i. e. one mole, of hydrogenated fish oil having an acid value of approximately two were transesterified by refluxing for one hour with 192 parts, i. e. six moles, of methanol, employing 8.3 parts of sodium as an alkaline catalyst. 44 parts of sulfuric acid were then added and esterification carried out by refluxing for four hours. After completion of the esterification reaction, 36 parts of calcium hydroxide were added to the reaction mixture. The reaction mixture was then filtered, the excess alcohol removed, and the glycerine separated from the esters. The crude glycerine was then heated with 64 parts of ammonium chloride at about 65° C. for approximately one hour. Any alcohol still associated with the glycerine was then removed by distillation, the glycerine filtered and then vacuum distilled at 2 mm. Excellent quality anhydrous glycerine in an amount equivalent to 75% of the theoretical yield was obtained.

Our process is particularly applicable for the refining of essentially anhydrous glycerine but it is obvious, of course, that it is also applicable to the refining of glycerine which is not essentially anhydrous. Consequently if it were desired, the process could be employed for refining crude glycerine obtained by the transesterification of fatty material employing a combined alkali and acid transesterification process even though such glycerine contained an appreciable amount of water. However, as has been pointed out above, the presence of large amounts of water in the glycerine considerably complicates the refining process.

In the specification and claims when reference is made to "neutralizing" the acidic glycerine or the acidic esterification mass with an alkaline earth oxide or hydroxide, the word "neutralizing" is used in the sense that sufficient of the alkaline earth compound is employed to completely react with all of the acidic material in the reaction mass. Thus the "neutralized" re-

action mass will actually have an alkaline pH. The reason for this is that an alkali metal hydroxide (the alkali metal cation coming from the alkaline catalyst employed in the transesterification) will be one of the end products of the reaction of the acidic material with the alkaline earth compound. It is true that there will be a point at which the glycerine or the esterification mass will have a neutral pH; however, the complete conversion of whatever alkali metal sulfate or phosphate is in the glycerine or in the esterification mass to the alkaline earth sulfate or phosphate necessarily produces a reaction mixture having an alkaline pH caused by the alkali metal hydroxide resulting from the "neutralizing" reaction.

Having described our invention what we claim as new and desire to secure by Letters Patent is:

1. In a process for refining glycerine obtained by transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterfied employing an acid catalyst, the steps comprising neutralizing the acidic glycerine with a compound selected from the group consisting of the alkaline earth hydroxides and oxides, heating the glycerine with an ammonium halide, and then separating the glycerine from insoluble material formed therein.

2. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with a compound selected from the group consisting of the alkaline earth hydroxides and oxides, removing insoluble material formed therein from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with an ammonium halide, and separating the treated glycerine from insoluble material formed therein.

3. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising separating the glycerine from the acidic esterification mass, neutralizing the acidic glycerine with a compound selected from the group consisting of the alkaline earth hydroxides and oxides, heating the glycerine with an ammonium halide, and separating the treated glycerine from insoluble material formed therein.

4. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with an alkaline earth hydroxide, removing insoluble material formed therein from the esterification mass, removing the majority of any excess unreacted alcohol from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with an ammonium halide, and separating the treated glycerine from insoluble material formed therein.

5. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with an alkaline earth hydroxide, heating the mass for a short time to aid in converting insoluble material in the mass into a more easily removable form, removing insoluble material formed therein from the esterification mass, removing the majority of any excess unreacted alcohol from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with an ammonium halide, extracting the halide treated glycerine at a temperature not above room temperature with a solvent selected from the group consisting of methanol, ethanol, propanol, butanol, and acetone, and recovering refined glycerine by removing the solvent from the solvent extracts.

6. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with an alkaline earth hydroxide, heating the mass for a short time to aid in converting insoluble material in the mass into a more easily removable form, removing insoluble material formed therein from the esterification mass, removing the majority of any excess unreacted alcohol from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with an ammonium halide, dissolving the halide treated glycerine in at least an equal weight of an aliphatic monohydric alcohol containing not more than 4 carbon atoms, adding acetone to the alcoholic solution until a precipitate just begins to form, heating the solution for a short time, removing insoluble material formed therein from the solution, and recovering refined glycerine by removing the solvent from the solvent solution.

7. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising separating the glycerine from the acidic esterification mass, neutralizing the acidic glycerine with a compound selected from the group consisting of the alkaline earth hydroxides and oxides, separating the glycerine from insoluble material formed therein, heating the glycerine with an ammonium halide, extracting the halide treated glycerine at a temperature not above about room temperature with a solvent selected from the group consisting of methanol, ethanol, propanol, butanol, and acetone, and recovering refined glycerine by removing the solvent from the solvent extracts.

8. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising separating the glycerine from the acidic esterification mass, neutralizing the acidic glycerine with a compound selected from the group consisting of the alkaline earth hydroxides and oxides, separating the glycerine from insoluble material formed therein, heating the glycerine with an ammonium halide, dissolving the halide treated glycerine in at least an equal weight of an aliphatic monohydric alcohol containing not more than 4 carbon atoms,

adding acetone to the alcoholic solution until a precipitate just begins to form, heating the solution for a short time, removing insoluble material formed therein from the solution, and recovering refined glycerine by removing the solvent from the solvent solution.

9. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with an alkaline earth hydroxide, removing insoluble material formed therein from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with ammonium chloride, and separating the treated glycerine from insoluble material formed therein.

10. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising separating the glycerine from the acidic esterification mass, neutralizing the acidic glycerine with a compound selected from the group consisting of the alkaline earth hydroxides and oxides, heating the glycerine with ammonium chloride, and separating the treated glycerine from insoluble material formed therein.

11. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with an alkaline earth hydroxide, removing insoluble material formed therein from the esterification mass, removing the majority of any excess unreacted alcohol from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with ammonium chloride, separating the treated glycerine from insoluble material formed therein, and distilling the glycerine under reduced pressure.

12. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with an alkaline earth hydroxide, heating the mass for a short time to aid in converting insoluble material in the mass into a more easily removable form, removing insoluble material formed therein from the esterification mass, removing the majority of any excess unreacted alcohol from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with ammonium chloride, extracting the ammonium chloride treated glycerine at a temperature not above about room temperature with a solvent selected from the group consisting of methanol, ethanol, propanol, butanol, and acetone, recovering refined glycerine by removing the solvent from the solvent solution, and distilling the glycerine under reduced pressure.

13. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising separating the glycerine from the acidic esterification mass, neutralizing the acidic glycerine with a compound selected from the group consisting of the alkaline earth hydroxides and oxides, separating the glycerine from insoluble material formed therein, heating the glycerine with ammonium chloride, extracting the ammonium chloride treated glycerine at a temperature not above about room temperature with a solvent selected from the group consisting of methanol, ethanol, propanol, butanol, and acetone, recovering refined glycerine by removing the solvent from the solvent solution, and distilling the glycerine under reduced pressure.

14. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with an alkaline earth hydroxide, heating the mass for a short time to aid in converting insoluble material in the mass into a more easily removable form, removing insoluble material formed therein from the esterification mass, removing any excess unreacted alcohol from the esterification mass, separating the glycerine from the esterification mass, heating the glycerine with ammonium chloride, dissolving the ammonium chloride treated glycerine in at least an equal weight of an aliphatic monohydric alcohol containing not more than 4 carbon atoms, adding acetone to the alcoholic solution until a precipitate just begins to form, heating the solution for a short time, removing insoluble material formed therein from the solution, recovering refined glycerine by removing the solvent from the solvent solution, and distilling the glycerine under reduced pressure.

15. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising neutralizing the acidic esterification mass with barium hydroxide, removing insoluble material formed therein from the esterification mass, separating the glycerine from the alkyl esters, heating the glycerine with ammonium chloride, separating the treated glycerine from insoluble material formed therein, and distilling the glycerine under reduced pressure.

16. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing an acid catalyst, the steps comprising separating the glycerine from the acidic esterification mass, neutralizing the acidic glycerine with barium hydroxide, separating the glycerine from insoluble material formed therein, heating the glycerine with ammonium chloride, separating the treated glycerine from insoluble material formed therein, and distilling the glycerine under reduced pressure.

17. In a process for refining glycerine obtained by the transesterification of a fatty material having an acid value of at least one wherein the fatty material is transesterified employing an alkaline catalyst and then esterified employing

an acid catalyst, the steps comprising separating the glycerine from the acidic esterification mass, neutralizing the acidic glycerine with barium oxide, separating the glycerine from insoluble material formed therein, heating the glycerine with ammonium chloride, separating the treated glycerine from insoluble material formed therein, and distilling the glycerine under reduced pressure.

18. A process in accordance with claim 11 wherein the alkaline earth compound which is employed is barium hydroxide.

19. A process in accordance with claim 12 wherein the alkaline earth compound which is employed is barium hydroxide.

20. A process in accordance with claim 14 wherein the alkaline earth compound which is employed is barium hydroxide.

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