May 2, 1950 S. STEINBERGER 2,506,473

METHOD OF OBTAINING FATTY ALCOHOLS FROM THEIR ESTERS

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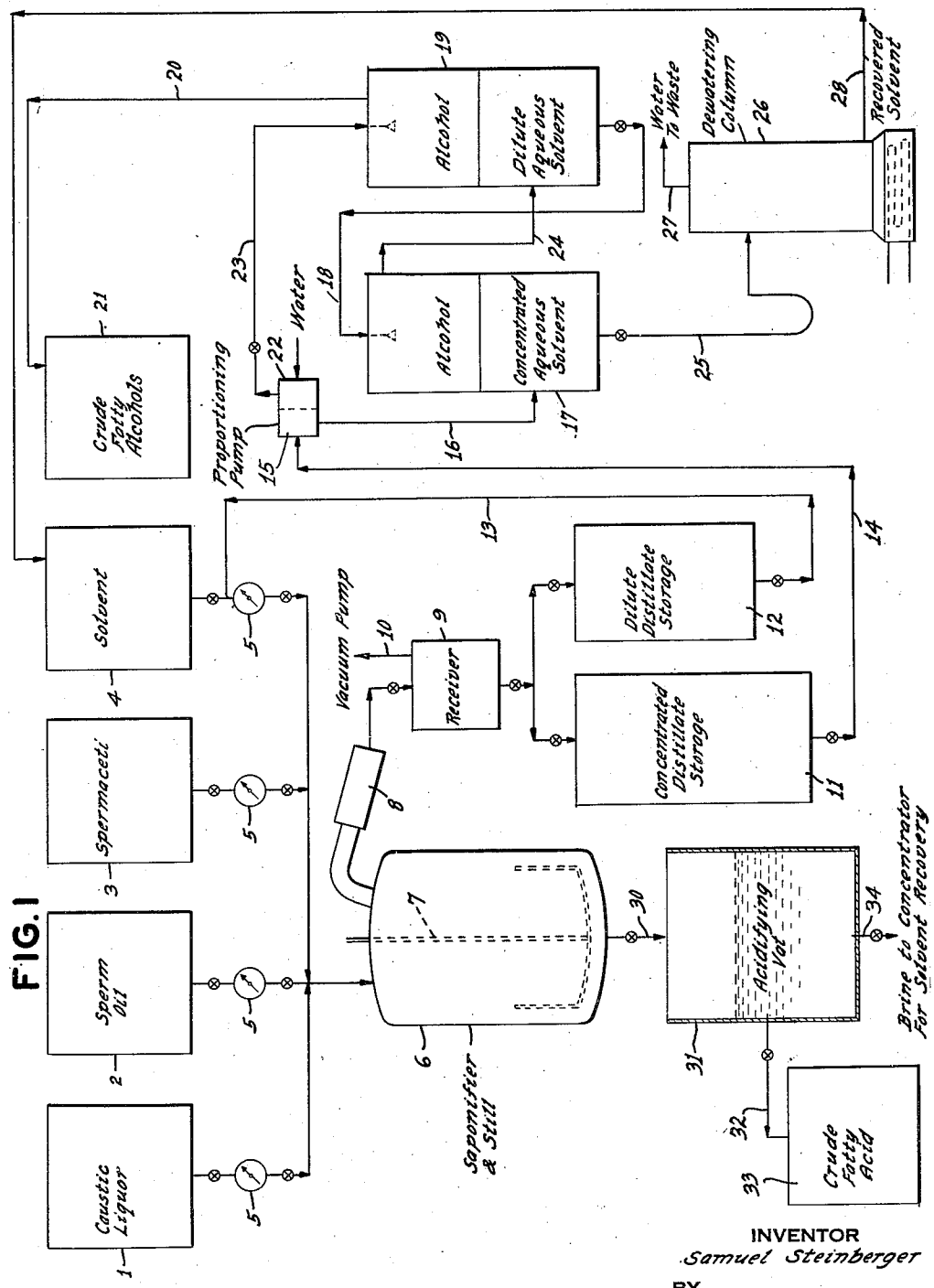


FIG. 1

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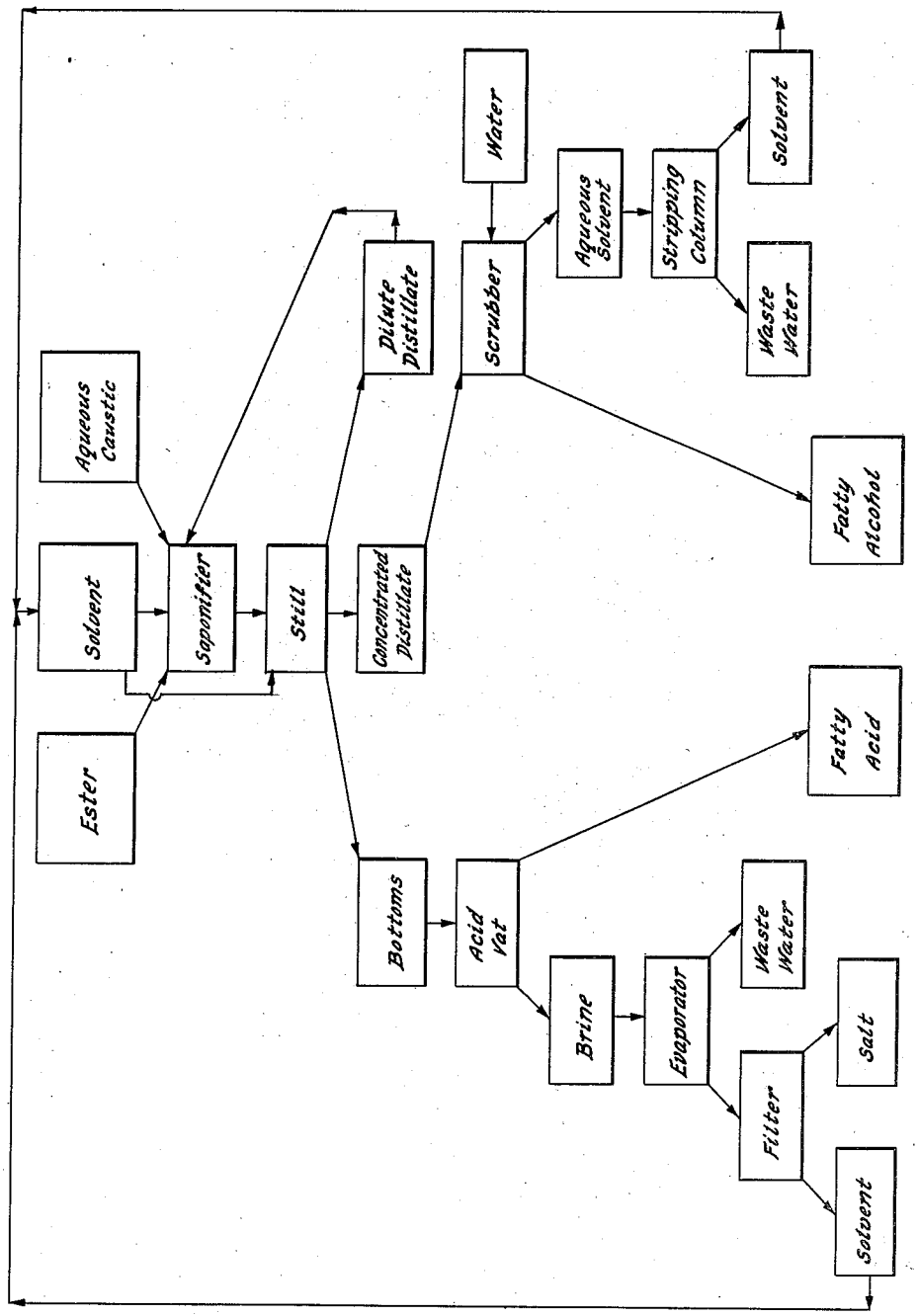
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FIG. 2



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METHOD OF OBTAINING FATTY ALCOHOLS FROM THEIR ESTERS

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12 Claims. (Cl. 260—638)

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This invention relates to an improved method for obtaining higher fatty alcohols from their esters as found in sperm oil, spermaceti, waxes, and other esters of alcohols containing 8 to 20 carbon atoms or more and including both natural esters (waxes, etc.) and synthetic esters of such high boiling fatty alcohols with fatty acids.

Heretofore the principal method for recovering such higher alcohols from their esters has consisted of saponifying the esters at necessarily elevated temperatures, with essentially anhydrous, strong alkalies such as caustic soda, caustic potash, or mixtures thereof or calcium hydroxide, followed by distillation with dry steam under reduced pressures and at relatively high temperatures. The still bottoms resulting from such distillation are usually of high softening point and high viscosity and must be removed from the still at an elevated temperature.

The present invention provides an improved process for obtaining higher fatty alcohols from their esters in which the successive operations of saponification, distillation and removal of residues are facilitated by the employment of a high boiling, water-miscible solvent which is a solvent for the fatty alcohols and the soap formed during the saponification, for example, an ether-alcohol such as triethylene glycol and the like.

The improved process in which such high boiling, water-miscible solvents are used has very practical advantages. The employment of such solvents lowers the temperature required for saponification and permits saponification to be effected within a reasonably short period of time and lowers the softening point of the residual soap mass resulting from the distillation of the fatty alcohols therefrom. The use of such high boiling solvents also promotes the distillation of the fatty alcohols from the saponified esters and gives a distillate containing both the fatty alcohols and solvent. The water-miscible properties of the high boiling solvent enables strong aqueous caustic alkali solutions to be employed for the saponification, as well as solid and essentially anhydrous alkalies. The utilization of such water-miscible solvents also permits alcohols to be separated from admixed high boiling solvent by adding water to form an aqueous-solvent layer in which the fatty alcohols are insoluble. The presence of the high boiling water-miscible solvents is also advantageous in the saponification residue, which can be diluted with water to form an aqueous solution of soap and solvent and then acidified to set free the fatty acid from the soap and form an aqueous solvent solution which also contains salt.

The present invention includes improvements in the saponification operation, in the distillation operation, in the residual soap treating operation, in the separation of distilled fatty alcohol from high boiling solvent, and in cyclic operations in which the high boiling, water-miscible solvent is separated from its aqueous solution for reuse in the process.

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The high boiling solvents used have boiling points or have a boiling point range similar to that of the higher fatty alcohols, for example, a boiling point range under ordinary atmospheric pressure of around 200 to 350° C. The high boiling solvents may have a boiling point somewhat higher than that of the fatty alcohol to be distilled or somewhat lower than that of the fatty alcohol. And where the ester saponified gives high boiling alcohols of different boiling points the solvent may have a boiling point higher or lower or between those of the alcohols. The high boiling solvents used have such a high boiling point that the distillation of the higher fatty alcohols is at a temperature such that the saponification mixture in the still is anhydrous, and the distillation results in the production of an anhydrous soap residue diluted with the high boiling solvent, while the mixed distillate of higher fatty alcohol and solvent is also anhydrous, except for the presence of some water which may be present during the saponification and which may be removed during the early portion of the distillation.

The solvents used are not only high boiling, but are also water-miscible. Among such high boiling water-miscible solvents are included various members of the group of ether-alcohols such as polyalkylene glycols and alkyl ethers thereof as well as high boiling water soluble polyamines such as polyalkylene polyamines, and alkylolamines such as triethanolamine. Among such high boiling solvents may be mentioned ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, butylene glycol, ethoxy triglycol, dimethoxytetraglycol, triethylene tetramine, tetraethylenepentamine, triethanolamine, amino ethyl ethanolamine, methyl diethanolamine, etc.

Where the fatty alcohols have a boiling point range around 200°, the high boiling water-miscible solvents advantageously have a similar boiling point. With esters such as those of sperm oil and spermaceti, the alcohols from which have higher boiling points, higher boiling solvents are advantageously used.

The solvents in some cases permit distillation of the fatty alcohol to take place at a temperature lower than that at which either the alcohol or the solvent alone will distill, apparently forming constant boiling mixtures. Even where such constant boiling mixtures are not formed the alcohol and solvent will be distilled together and the distillation of the solvent will promote or facilitate the distillation of the alcohol.

The solvents used promote the saponification,

facilitating the use of alkali metal hydroxides which are soluble in the solvents or strong solutions of which are readily miscible with the solvents so that the presence of a solid phase saponifying reactant is eliminated. As a result it is possible to carry out the saponification in the presence of such solvents in a relatively short period of time, for example, in three hours or less, and at relatively low temperatures, varying from temperatures somewhat less than to temperatures not greatly exceeding that of boiling water.

An advantageous method of carrying out the process is by using strong aqueous solutions of sodium or potassium hydroxide instead of the solid and essentially anhydrous alkalies. With water miscible high boiling solvents the saponification can be carried out by employing such strong, aqueous caustic solutions without appreciably affecting the saponification rate or the quality of the saponification, while the mixing and handling of the reaction mixture is facilitated.

The saponification step and the subsequent distillation step of the process can be carried out in the same vessel which will serve first as a reaction vessel at a lower temperature and later as a still at a higher temperature. The total processing time may be reduced in this case by beginning the distillation before the saponification is completed, with the two processes proceeding simultaneously. The apparatus or vessels or stills employed will be provided with suitable heating means and with stirrers or agitators. Where saponification is carried out in one vessel and distillation in another, the saponification may be completed before the distillation begins or the incompletely saponified charge may be transferred to the still and the saponification completed during the early period of distillation.

The distillation of the high boiling fatty alcohols is carried out at pressures below atmospheric in order to take advantage of the low temperatures at which the charge may be maintained in the fluid state as well as to insure greater heat economy. Other things being equal, the degree of vacuum required is preferably that which will yield a high ratio of fatty alcohol to solvent in the distillate.

In general the amount of solvent present in the saponification step may be kept to a minimum, with the use of sufficient solvent to give a thinly fluid mixture for saponification, but without undue dilution of the reaction mixture with solvent. During the course of the distillation, however, more solvent is advantageously added as required to make up for that which is distilled with the fatty alcohol and to insure that all of the fatty alcohol is distilled from the charge. Practically quantitative yields of alcohol could be obtained. During the early or main portion of the distillation a high ratio of fatty alcohol to solvent is distilled. After most of the fatty alcohol has been distilled, and during the last portion of the distillation, the distillate is largely solvent; and this portion of the distillate is advantageously set aside and reused in a succeeding batch. The distillation is remarkable for its almost complete freedom from foaming until the still bottoms contain a low concentration of solvent. The distillation residue can be freed from most of its solvent but sufficient solvent should be left to insure that the residue is still fluid when cooled. The distillation residue

is an anhydrous soap diluted with anhydrous solvent.

After the distillation, the residue in the still is cooled to a point where it is still fluid, which is the case at moderate temperatures, and the process is in this respect distinguished from processes carried out in the absence of a solvent where the residue is highly viscous even at 200° C. or higher in the case of spermaceti. After cooling the fluid, anhydrous residue is added to aqueous acid, or is added to water with subsequent addition of acid, to set free the fatty acids which separate as a layer on top of the aqueous solvent layer. The water-miscible solvent readily mixes with the added water. Any solvent separating with the fatty acids is readily washed out to give a substantially solvent-free fatty acid layer. The aqueous solvent mixture containing salt from the acidification of the soap is advantageously treated thereafter to recover the solvent for reuse.

The distillate is advantageously collected in two separate parts, the first and main part containing most of the fatty alcohol mixed with anhydrous solvent; and the latter part being mainly solvent with a small amount of fatty alcohol. This second amount of anhydrous solvent with a small amount of fatty alcohol is advantageously returned to the process and used as a solvent in treating a further batch of ester. The main portion of the distillate is advantageously treated by adding water which extracts the solvent and separates the insoluble fatty alcohol, giving a fatty alcohol layer and an aqueous solvent layer. The fatty alcohol fraction, after washing with fresh water, is of a high grade. The aqueous solvent mixture is then distilled to remove the water and give anhydrous solvent for return to the process.

The separation of the solvent and fatty alcohol can be carried out by the use of organic materials such as ligroin, etc. which exert a selective solvent action and extract the alcohol from the high boiling solvent. But for practical operation the use of water to separate the water-miscible high boiling solvent from the high boiling fatty alcohol is a more advantageous method.

The nature of the process will be further described in connection with the accompanying drawings which illustrate, in a somewhat conventional and diagrammatic manner, in Fig. 1, an arrangement of apparatus and processing steps, and in Fig. 2, a flow sheet, but it will be understood that the invention is not limited thereto.

Referring to the diagrammatic arrangement shown in Fig. 1, a caustic liquor supply tank is conventionally shown at 1, supply tanks for ester at 2 and 3, for sperm oil and spermaceti, respectively, as the esters to be treated and a solvent supply is indicated conventionally at 4. These supply tanks are connected through pipe connections having control valves therein and meters 5 therein to the saponifier and still 6, having stirrer 7 therein and provided with heating means (not shown). The arrangement is such that a suitable charge of ester such as sperm oil or spermaceti with an appropriate charge of caustic liquor and solvent can be supplied initially to the saponifier for the saponification step of the process; and additional solvent can be supplied as required during the subsequent distillation step.

The distillate from the still 6 is condensed in the condenser 8 and collected in the receiver 9

which is connected through the line 10 with a vacuum pump (not shown) by which a high vacuum can be maintained on the still during distillation. From the receiver 9 the main portion of distillate containing most of the high boiling fatty alcohol is collected in the concentrated distillate storage receptacle 11, while the latter part of the distillate containing mainly solvent and with a small amount of fatty alcohol is collected in the dilute distillate storage tank 12 and returned through the line 13 to be added to the solvent in the tank 4, so that this solvent can be used over again in a subsequent charge and its fatty alcohol content subsequently recovered.

The concentrated distillate in the form of an anhydrous mixture of high boiling solvent and high boiling fatty alcohol passes from the tank 11 through the line 14 to the proportioning pump 15 and then through the line 16 to the bottom of the tank 17, where dilution takes place with separation of alcohol and a concentrated aqueous solvent layer. The alcohol passes through line 24 to the bottom of a second separating tank 19 where the alcohol is further washed with water to remove solvent from it and the resulting crude fatty alcohols pass through the line 20 to the storage tank 21.

Water is supplied through the proportioning pump 22 and passes through the line 23 to the top of the tower 19 where the fresh water serves to wash the fatty alcohol passing upwardly therethrough, to remove water-miscible solvent from it. The resulting dilute aqueous solvent solution passes through the line 18 to the top of the tower 17 where it serves to effect the preliminary separation of the solvent-alcohol mixture into an upper alcohol layer and a lower layer of concentrated aqueous solvent. The concentrated aqueous solvent is drawn off through the line 25 to the dewatering column or still 26, where the mixture is heated and water distilled through the line 27 and from which the resulting anhydrous solvent is returned through the line 28 to the solvent storage tank 4.

After the distillation of the fatty alcohol from the still is completed, and after part of the remaining solvent has been removed from the still, the residue, made up of the anhydrous soap and sufficient solvent to give a liquid mixture, is discharged through the line 30 to the acidifying vat 31 where it is treated with acidified water to set free the fatty acids from the soap, and to form an aqueous solvent layer containing the salt formed. The crude fatty acids are drawn off through the line 32 to the crude fatty acid storage tank 33. The brine containing the salt and the organic solvent in aqueous solution is drawn off through the line 34 and is also subjected to concentration to distill the water from it and to separate the salt from it and to give solvent which can also be returned for further use in the process.

In the apparatus and diagrammatic arrangement of process steps illustrated and above described, and in the flow sheet of Fig. 2, the solvent and caustic will be charged to the agitated saponification kettle through meters or weighing tanks and heated and the ester from the storage tank added and the saponification then conducted more or less to completion. In the arrangement shown in Fig. 1 the mass is distilled in the same vessel, although it could be transferred to a separate still as shown in Fig. 2, or stored for treatment in a continuous

distillation system. The distillate is diverted either in the concentrated storage tank for further treatment to separate the fatty alcohol from the solvent and to recover the solvent for reuse; or, in the later stages of distillation the distillate may be diverted into the tailings or dilute distillate storage receiver from which solvent for the next saponification batch may be drawn, or returned to the saponifier as shown in Fig. 2. In the course of the distillation additional solvent will be drawn from the storage tank as required to replace the solvent driven off with the fatty alcohol and to insure that the charge in the still is freed from all of the fatty alcohol. The residue from the still may then be cooled as desired and dropped into the acidified water to liberate the fatty acids from the soap and to give a crude fatty acid as one of the products of the process. The lye or brine from which the fatty acids are separated and which contain salts, water and solvent may be concentrated to remove water and precipitate the salts and to recover the solvent for reuse.

The concentrated distillate from the still may be treated with water either batchwise or continuously to separate fatty alcohols from the solvent. In the arrangement shown in Fig. 1 the distillate is passed successively through the countercurrent extraction towers 17 and 19 against water with regulation of the amount of water and distillate by the proportioning pump. The washed, crude alcohol goes to the storage tank from which it may be removed for drying, fractionation or immediate use. The diluted solvent is then passed through the concentrating column where it is freed from water and the solvent recovered and returned to the process.

The cyclic nature of the process and the interrelation of the various steps when carried out in a cyclic manner is illustrated in the drawings. It will be seen that the same high boiling, water-miscible solvent is recovered and used in a cyclic manner. From the drawings, and from the foregoing description, it will be seen that the high boiling solvent is added and is present during saponification to promote the saponification; that it is also present and is used during the distillation to promote the distillation; and that advantage is taken of the water-miscible properties of the solvent to facilitate separation of the fatty alcohols therefrom and also to facilitate the acidification of the soap and the recovery of fatty acids therefrom; while the solvent, separated as an aqueous solution, is freed from water and returned to the process in a cyclic manner.

The invention will be further illustrated by the following specific examples but is not limited thereto.

Example 1.—A mixture of 400 parts of triethylene glycol and 40 parts of 48° Bé. NaOH (assaying 47.1% NaOH and 0.8% Na_2CO_3) was heated to 80° C., whereupon 200 parts of spermaceti was added gradually. The mixture was then heated with agitation to 90–95° C. for one and one-half hours. Titration of an aliquot at this point indicated that the saponification was essentially complete.

202 parts of the mixture containing 28.4 parts of fatty alcohols was transferred to a distilling vessel and distilled at a pressure of 8–12 mm. absolute. Additional glycol was added at intervals. A first cut distilling between 146° and 160°, and amounting to 122 parts, contained 19.9 parts or 70% of the theoretical. Further cuts, total-

ling 183 parts, brought the recovered alcohol to 28.4 parts, or approximately 100%.

To the above distillate, water was added sufficient to bring the glycol concentration to a 70% aqueous solution (70% solvent and 30% water); the alcohols separated almost quantitatively from the solution, and contained only a small amount of glycol and water. This was removed by a second wash.

Example 2.—To a mixture of 330 parts of tetraethylene glycol and 54 parts of 40% aqueous NaOH at 70° C., 210 parts of sperm oil was added gradually, and the mixture was heated to 90° C. for about two hours. Saponification was essentially complete.

To 550 parts of this product corresponding to 196 parts of sperm oil, was added 100 parts more tetraethylene glycol, and the mixture was distilled at a pressure of 16±2 mm., between 180° and 205° C. 95 parts of distillate contained 37 parts of fatty material. As the distillation proceeded, more of the glycol was introduced; successive cuts contained 42.2 parts more of fatty material, totaling 40.3% of the sperm oil taken.

Addition of water to the distillate caused a separation into two layers, the upper of which contained practically all of the fatty alcohols.

Example 3.—210 parts of sperm oil, 400 parts of triethanolamine and 54 parts of 40% NaOH were heated for one and one-half hours at 90–100° C. Distilled at 15–16 mm. between 186–207° C. a main fraction containing 42% of fatty alcohols, amounting to 37.5% of the sperm oil taken, was removed; further distillation yielded a less concentrated cut, bringing the total yield to 41.8% on the weight of the sperm oil.

Addition of water to the distillate caused a separation into two layers, the upper of which contained practically all of the fatty alcohols.

The above examples illustrate the saponification and distillation steps of the process and the separation of the fatty alcohols from the high boiling water-miscible solvent. The recovery of the solvent for reuse and the acidification of the soap to recover fatty acids are not included in the above examples.

It will thus be seen that the present invention provides an improved method for recovering high boiling fatty alcohols from their esters in which high boiling water-miscible solvents are used to promote the saponification and subsequent distillation; and that such solvents are advantageously used in a cyclic manner. It will further be seen that the use of such high boiling water-miscible solvents has many advantages in promoting the saponification and distillation as well as the subsequent treatment of distilled residue and the recovery of the distillate, advantage being taken of both the high boiling properties of the solvents during the distillation and of the water-miscible properties of the solvents to promote separation of the reaction products.

I claim:

1. The method of recovering high boiling fatty alcohols containing 8 to 20 carbon atoms or more from their esters which comprises saponifying such esters with an alkaline agent in the presence of a water-miscible solvent which is a solvent for the fatty alcohols and soap formed by the saponification and which has a boiling point within the range from about 200 to about 350° C., and then distilling the mixture to obtain a co-distillate containing such solvent and the fatty alcohols.

2. The improvement in the method of recovering of fatty alcohols containing 8 to 20 carbon atoms from their esters by saponifying such esters with an alkaline agent and then distilling the alcohol from the saponification mixture, which comprises promoting the distillation of the fatty alcohol by carrying out such distillation of the saponification mixture with a water-miscible solvent which is a solvent for the fatty alcohols and soap formed by the saponification and which has a boiling point within the range from about 200 to about 350° C., to obtain a co-distillate containing such solvent and the fatty alcohols.

3. The process according to claim 1 in which the co-distillate of water-miscible solvent and fatty alcohols is treated with water to separate the fatty alcohols and form an aqueous solvent mixture and in which the solvent is recovered from such aqueous mixture by distillation for further use in the process.

4. The process according to claim 1 in which the residue from the distillation, in the form of an anhydrous mixture of soap and solvent, is treated with acidified water to set free the fatty acids and form an aqueous-solvent-salt mixture, followed by separation of the solvent from the water and salt and return of the solvent to the process.

5. The process according to claim 1 in which the co-distillate of solvent and fatty alcohols is obtained in the form of a co-distillate with a high content of fatty alcohols and a final distillate of solvent with a small amount of fatty alcohols, with return of the second distillate for use as a solvent in the further carrying out of the saponification step of the process.

6. The process according to claim 1 in which the co-distillate of solvent and fatty alcohol is treated with water to separate the fatty alcohol and form an aqueous-solvent mixture by passing the distillate through successive treatments of counter-flow with water to form a concentrated aqueous solution of the solvent and to wash the alcohol free from solvent, followed by distillation of the aqueous solvent and return of the resulting anhydrous solvent to the process.

7. The process according to claim 1 in which the water-miscible solvent is a polyalkylene glycol solvent.

8. The process according to claim 1 in which the water-miscible solvent is a polyalkylene glycol ether solvent.

9. The process according to claim 1 in which the water-miscible solvent is triethylene glycol.

10. The process according to claim 1 in which the water-miscible solvent is a polyamine.

11. The process according to claim 1 in which the water-miscible solvent is an alkylolamine.

12. The process according to claim 1 in which additional solvent is admixed with the mixture being distilled in order to maintain such mixture in a fluid condition without undue dilution of said mixture.

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