

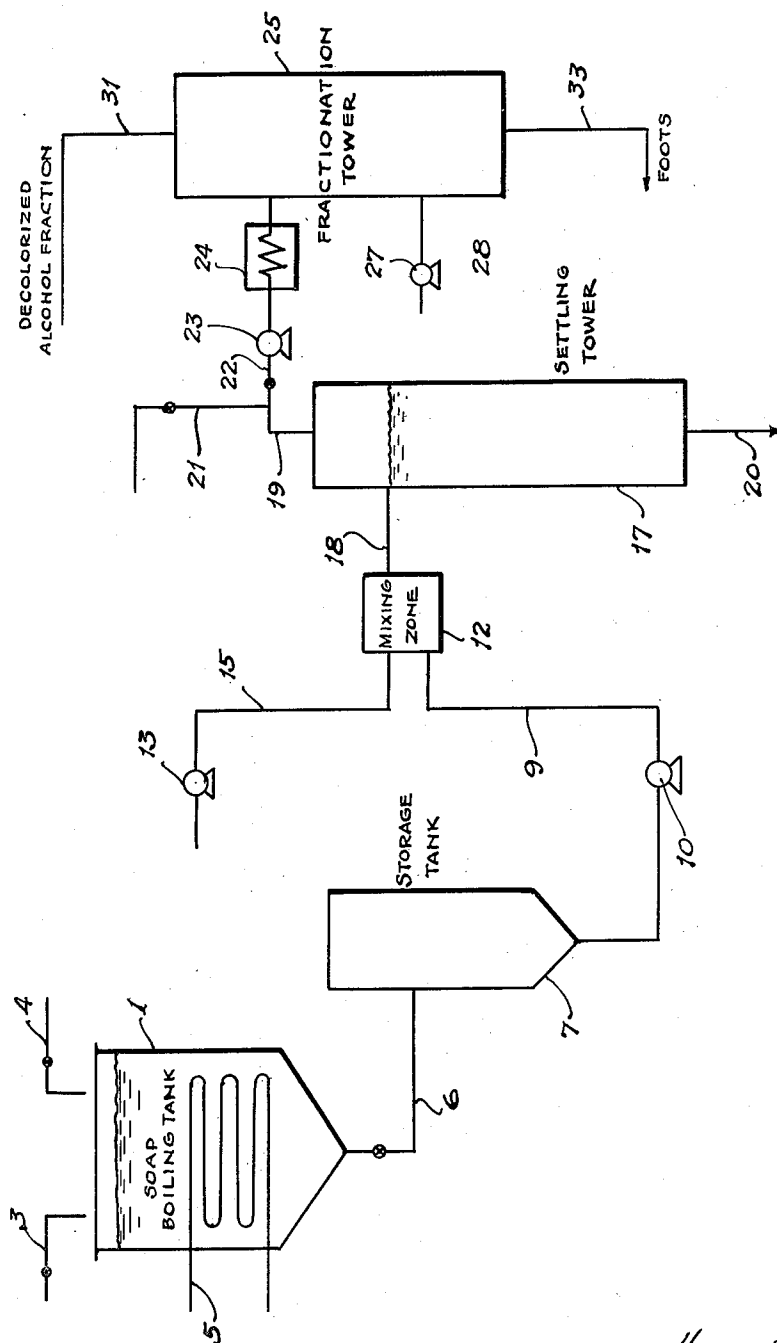
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MANUFACTURE OF HIGHER ALCOHOLS

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MANUFACTURE OF HIGHER ALCOHOLS

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This invention relates to a method for the separation of higher alcohols from natural waxes. More particularly it provides an improved process for the complete recovery of higher alcohols from saponified natural waxes. The invention will be described in connection with the recovery of cetyl alcohol from crude sperm oil as representatively falling within the scope of the invention.

In the past, cetyl alcohol has been produced from crude sperm oil and spermaceti by distillation of the alcohol from the saponified crude oil or wax. Distillation temperatures of around 200° C. to 250° C. at 10 to 15 millimeters pressure are employed. Under these severe operating conditions, the soap which is formed during the saponification reaction hardens and discolors to the extent that extensive refining operations of the soap or of the fatty acids recoverable therefrom are made necessary in order to obtain a usable product. Moreover, the higher alcohol obtained by this distillation method is of relatively poor quality because of severe operating temperatures required and must be subjected to bleaching, refining, and deodorization to produce alcohol of sufficiently high quality for use as an emulsifying agent in cosmetic products, which is one of the major uses for this material. The refining operations, in addition to being time-consuming, entail considerable loss.

An object of the invention is to produce a high quality higher alcohol by a low temperature process whereby extensive refining is unnecessary.

Another object of the present invention is to provide a process for the separation of higher alcohols from saponified waxes under such conditions that the soap or the fatty acids recoverable therefrom are readily usable and free from polymerized and colored material.

A still further object of the invention is to provide a method whereby the alcohols extracted from saponified waxes can be readily fractionated according to their degree of unsaturation.

In accordance with the invention, it is contemplated to saponify a natural wax with caustic alkali, such as sodium hydroxide, potassium hydroxide, or calcium hydroxide, to obtain a mixture of soap and higher alcohol. This step is effected with a minimum of water and at elevated temperatures, usually exceeding 230° F. The saponified mixture of soap and alcohol is then extracted with a normally gaseous hydrocarbon, such as propane, by introducing the saponified mixture and solvent into an extraction zone wherein the alcohols are dissolved in the liquid

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propane and the soap and moisture rapidly gravitate to the bottom of the extraction vessel. The alcohol-propane solution, because of its low specific gravity of about 0.5 to 0.6, depending on temperature and pressure conditions, separates readily from the soap and moisture. The solution of solvent and alcohol can either be fractionated further at different temperatures and pressures or the alcohol can be recovered immediately by subjecting the solution to a solvent recovery process.

To further illustrate the operation of the invention, reference is made to the figure which schematically represents one method of carrying out our invention.

Referring to the figure, sperm oil or other waxy material may be introduced through line 3 into a soap kettle 1 equipped with a suitable heating coil 5. A saponifying agent, such as caustic soda solution of about a 40 per cent concentration, is introduced into kettle 1 through line 4. An excess of alkali, for example about 10 per cent, is used to ensure complete saponification. The oil and caustic are boiled until complete saponification is obtained, which usually requires 4 to 6 hours. The saponification reaction products are then led through line 6 to a soap stock feed tank 7 which is equipped with a steam jacket or other suitable means of supplying heat to maintain the soap product mixture in suitable condition for pumping. The soap stock is pumped through line 9 by pump 10 into mixing zone 12. Propane is pumped into mixing zone 12 by pump 13 through line 15. The amount of propane and the temperature thereof are preferably such as to dissolve substantially all of the alcohol liberated by the saponification reaction. Solvent ratios of about 3 to 1 to 10 to 1 at temperatures from about 100° F. to 150° F., with corresponding pressures of 225 to 300 pounds per square inch to maintain the solvent in liquefied condition, have been found to be satisfactory operating conditions in the mixing zone. The mixed streams are introduced into a settling tower 17 through line 18 wherein a rapid and complete settling of the soap, water, and excess caustic is accomplished. The propane and alcohol solution is withdrawn through line 19, while soap, water, and excess caustic solution are removed from the settling zone through line 20. The propane-alcohol solution can be immediately taken through line 21 to a solvent recovery unit not shown and the solvent stripped from the alcohol. Alternatively, the alcohol propane solution is pumped through

line 22 by pump 23 through a heater 24 into the upper section of fractionation column 25. Additional propane is introduced simultaneously by pump 27 through the line 28 into the lower section of the fractionation tower, the amount of solvent varying from about 10 to 1 to 40 to 1. The fractionation tower is maintained at temperature and pressure conditions such that a separation of the extracted alcohols into two fractions is obtained. Depending upon the desired fractionation, the temperature varies from about 160° F. to as much as about 205° F., with a corresponding pressure range of from about 450 pounds to 700 pounds per square inch. A temperature gradient of from about 3° to 8° F. is preferably maintained in the column. The overhead fraction which always contains the majority of the solvent is withdrawn through line 31 and conducted to a solvent recovery system not shown. The bottom fraction is withdrawn from the fractionation tower through line 33 to a smaller solvent recovery system not shown.

As an example of the operation of our invention, crude spermaceti, obtained by the cold pressing of sperm oil, having an iodine value of 30 and a saponification value of 126, was saponified by boiling with a 10 per cent excess of a 50 per cent caustic soda solution for 8 hours. The reaction product was then mixed with 5 volumes of liquid propane at a temperature of 120° F. and 275 pounds of pressure and introduced into a settling tower wherein a complete and rapid settling of the water, soap, and excess caustic was effected. The supernatant propane solution was withdrawn from the upper portion of the settling tower and pumped into the upper portion of a packed fractionation column, while an equal volume of propane was introduced into the lower third of the tower. A temperature gradient of 4° F. was maintained throughout the column, the overhead take-off temperature being 194° F., and the bottom take-off temperature, 190° F. Under these conditions an overhead fraction containing about 40 per cent of the alcohol and a majority of the solvent was obtained. Upon removal of the solvent, the alcohol in the overhead fraction had an iodine value of 2 and for all practical purposes was water-white and was substantially pure cetyl alcohol. The higher alcohol in the lower phase was substantially darker in color and had an iodine value of about 55.

As a further illustrative example of our invention, carnauba wax of an iodine value of 13.5 and a saponification value of 82 was saponified by boiling with a 40 per cent excess of a 50 per cent solution of caustic potash. The saponified mixture was mixed with 5 volumes of liquid propane at a temperature of 130° F. and a pressure of 300 pounds. The mixture was introduced into a settling zone to effect the separation of the water, soap, and excess caustic. The supernatant solution of higher alcohol in propane was taken directly to a solvent recovery unit and the propane removed from the alcohols. The alcohols obtained showed a saponification value of about 1 and had an iodine value of 5.

The soap obtained from the settling process was sufficiently light in color to make it readily available for use in blending with regular kettle boiled soaps. In the present example, the soap and caustic solution obtained was used with a liquid soap made by the saponification of an 80-20 blend of olive oil and coconut oil. Propane-settled soap was added to the soap kettle at the beginning of the soap boiling operation,

so that the excess caustic was utilized for the saponification of the olive oil-coconut oil blend as added.

Our invention is likewise applicable to the separation of long chain alcohols present in other natural waxes such as beeswax, candelilla, montan, and others. Cetyl alcohol, however, has a much wider commercial application than the other naturally occurring higher alcohols and the process herein described is especially useful for the preparation of highly purified cetyl alcohol from the rendered fat of the sperm whale.

In addition to propane, other solvents which show selective solvent action at temperatures and pressures near the critical points may be used. Examples of such solvents are ethane, butane, propylene, butylene, and mixtures of these solvents.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the treatment of waxes containing saturated and unsaturated esterified alcohols, which comprises, saponifying the wax to obtain soap and the alcohols, subjecting the saponification products while fluid in the presence of a liquefied normally gaseous hydrocarbon to an elevated temperature and superatmospheric pressure whereby two fractions are formed, the lower of said fractions containing soap and the other containing the alcohols, subjecting the latter fraction to increased pressure and temperature in the presence of additional liquefied normally gaseous hydrocarbon whereby two phases are obtained, the upper of which is relatively rich in saturated alcohols, and separating the phases.

2. The process substantially as described in claim 1 wherein the liquefied normally gaseous hydrocarbon is propane.

3. The process substantially as described in claim 1 wherein the wax is spermaceti.

4. In a process of recovering substantially pure higher alcohols from natural waxes which have been saponified, the improvement which comprises: treating a saponified natural wax containing the higher alcohols, water, and excess alkali by admixing while in a fluid condition with a liquefied normally gaseous hydrocarbon, said liquefied hydrocarbon being a solvent for the higher alcohols without dissolving the saponified material, water, and excess alkali; separating the undissolved materials from the liquefied hydrocarbon solution containing the dissolved higher alcohols; contacting the said liquefied hydrocarbon solution with additional liquefied normally gaseous hydrocarbon in a fractionating zone at a temperature and pressure substantially greater than was employed in the admixing step to form upper and lower liquid phases, the upper of said phases comprising the major proportion of the liquefied hydrocarbon containing substantially pure higher alcohols; and recovering the said higher alcohols from the said upper phase.

5. In a process of recovering substantially pure higher alcohols from natural waxes which have been saponified, the improvement which comprises: mixing a saponified natural wax containing the higher alcohols, water, and excess alkali while in a fluid state with from approximately three to ten times its volume of a liquefied nor-

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mally gaseous hydrocarbon at a temperature between approximately 100° F. and 150° F. at a pressure of between approximately 225 and 300 pounds per square inch, said liquefied hydrocarbon being a solvent for the higher alcohols without dissolving the saponified material, water, and excess alkali; separating the undissolved materials from the liquefied hydrocarbon solution containing the higher alcohols; contacting the said liquefied hydrocarbon solution with additional liquefied normally gaseous hydrocarbon in a fractionating zone to increase the hydrocarbon ratio to between approximately 10:1 and 40:1 at a temperature of between approximately 160° F. and 205° F. and a pressure of between approximately 450 and 700 pounds per square inch to form upper and lower liquid phases, the upper of said phases comprising the major proportion of the liquefied hydrocarbon containing substantially pure higher alcohols; and recovering the said higher alcohols from the said upper phase.

6. In a process of recovering substantially pure cetyl alcohol from crude spermaceti which has been saponified, the improvement which comprises: mixing the saponified spermaceti containing cetyl alcohol, water, and excess alkali with approximately five times its volume of liquefied propane at a temperature of approximately 120° F. and a pressure of approximately 275 pounds per square inch; separating the liquefied propane solution containing a substantial proportion of the cetyl alcohol from the undissolved materials; contacting the said liquefied propane solution in a fractionating zone with approximately an equal volume of propane at a temperature of approximately 194° F. and a pressure of approximately 600 pounds per square inch to form upper and lower liquid phases, the upper of said phases comprising the major proportion of the propane containing substantially pure cetyl alcohol; and recovering substantially pure cetyl alcohol from the said upper phase.

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7. In a process of recovering a higher alcohol from waxes containing an esterified higher alcohol, the steps which comprise: saponifying the wax with an alkali to form a soap and a higher alcohol, subjecting the aqueous saponified mixture while in the fluid state to treatment with a solvent comprised essentially of a liquefied normally gaseous hydrocarbon at an elevated temperature and superatmospheric pressure without altering the composition of the aqueous saponification mixture, thereby forming an upper phase which is relatively rich in a higher alcohol and a lower phase which is relatively rich in soap, and separating the respective phases.

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