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(54) SEPARATION OF ALCOHOL HYDROCARBON MIXTURES

(54) SEPARATION DE MELANGES D'HYDROCARBURE ET D'ALCOOL

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ABSTRACT:

CLAIMS: [Show all claims](#)

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This invention relates to improvements in the separation of oxygen-containing compounds from their mixtures with hydrocarbons.

As is known, suitable conditions may be selected for effecting the catalytic hydrogenation of carbon monoxide, so that the primary products obtained contain, in addition to the hydrocarbons, increased yields of oxygen-containing compounds such as alcohols, esters, aldehydes, acids, etc. These oxygen-containing compounds must, of course, be separated from the mixtures obtained for further processing. The esters present cause considerable difficulties in the separation of these mixtures. A selective extraction or azeotropic distillation can be used for this purpose only with considerable difficulty, due to the presence of these esters.

In order to overcome these difficulties, it has been proposed to split the esters by treatment with potash solution or caustic soda solution to form salts of fatty acids and alcohols. According to one such proposal, the saponification is effected at elevated temperature and at a pressure sufficient to prevent evaporation of the components of the mixture. After the saponification, the pressure is released and the vaporizable portions will thus be distilled from the reaction mixture. These proposals, however, have not met with much success with the use of caustic soda solution, due to the formation of solid soaps, which, especially with the long-chained hydrocarbons, form emulsions, so that it is difficult to separate them from the reaction products. The use of a caustic soda solution for this purpose would be very advantageous in commercial operation, due to its relatively low cost.

One object of this invention is the separation of oxygen-containing compounds from their mixtures with hydrocarbons without the above-mentioned disadvantages.

A further object of this invention is to effect such a separation with a saponification, using inexpensive sodium hydroxide. These, and still further objects, will become apparent from the following description:

In accordance with the invention, alcohol hydrocarbon mixtures, and especially such mixtures obtained from the catalytic hydrogenation of carbon monoxide, are separated by saponification with sodium hydroxide at an elevated temperature and at a pressure sufficient to prevent evaporation of the components of the mixture. It has very surprisingly been found that by using a quantity of sodium hydroxide not in excess of 20% of the theoretical quantity required, based on the ester number and the neutralization number of the mixture, and filtering the precipitated metal oxides, under pressure, if necessary or desired, and separating the aqueous alkaline layer with the water-soluble alcohols from the upper layer at the temperatures used for the ester splitting, none of the disadvantages previously encountered with the use of sodium hydroxide occur, and the separation may be effected in a particularly advantageous manner. The neutralization and splitting of the acids and esters present by saponification with sodium hydroxide must be effected with at least 140% of the theoretical quantity required based on the ester number and neutralization number of the mixture, and must not be effected with a quantity greater than 20% in excess of the theoretical quantity required.

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It has been found particularly advantageous in accordance with the invention, if the esters are split with the caustic soda solution in the presence of lower alcohols having 2 to 5 carbon atoms. These alcohols have been found to facilitate the dissolving between the aqueous caustic soda solution and the water-insoluble esters by promoting the formation of an emulsion. After the completion of the reaction, however, very surprisingly the alcohol acts as a demulsifier, which is very desirable and necessary at that time. The presence of these alcohols is therefore desirable during the ester splitting and after the ester splitting, so that they should be added if required to the mixture before the splitting is effected.

In accordance with one suitable mode of operation, the entire alcohol hydrocarbon mixture, including the reaction water resulting from the carbon monoxide hydrogenation, is stirred into an emulsion with the quantity of sodium hydroxide required for the splitting and neutralization. This is effected with the addition of the lower alcohols having from 2 to 5 carbon atoms if necessary or desired.

After the splitting an upper oily layer is formed. This upper oily layer is drawn off from the alkaline aqueous layer and suitably washed with preheated water under pressure at the temperature of the ester splitting. The washing is suitably followed by a second washing effected under the same conditions with a washing water to which 30 to 50 parts of at least one water-soluble lower alcohol having a molecular size of up to 5 carbon atoms, as, for example, methyl alcohol, ethyl alcohol, propyl alcohol, etc. has been added. If required, the layer may be subjected to a final washing with

pure water under pressure. After this washing the oily layer may be subjected to a normal pressure distillation, followed by a vacuum distillation.

5 In accordance with the invention, the yield of alcohols may be increased by subjecting the olefins still present in the oily layer, which is freed, if necessary or required, from solid paraffin to the so-called Oxo synthesis. The olefins will thus be converted in the known manner into aldehydes by the catalytic addition of carbon monoxide and  
10 hydrogen at elevated pressure and elevated temperature, i.e., they are formylated. The aldehydes so obtained may be converted into alcohols by hydrogenation in the known manner.

The alcohols recovered may be separated from the  
15 remaining saturated hydrocarbons in any conventional manner, as, for example, by a selective extraction or by azeotropic distillation.

The water-insoluble raw alcohols separated in the above-described manner from the hydrocarbons still contain  
20 partially unsaturated alcohols and ketones. By a hydrogenation under mild hydrogenation conditions, these unsaturated alcohols may be converted into saturated alcohols. At the same time, the ketones will be converted into secondary alcohols.

25 The separation of the alcohols recovered by this mild hydrogenation from any hydrocarbons still present in small quantities, may suitably be effected by dissolving them in alcohol-water mixtures, and freeing them from the residual hydrocarbons by a distillative separation of a part of the  
30 alcohol-water mixture.

The aqueous alkaline solution which will form as the lower layer after the ester splitting, is cooled, which will result in the formation of two layers. The newly formed upper layer contains higher alcohols and is separated. The remaining layer contains the combined alkaline washing and reaction waters and may be subjected to a distillation for the recovery of the water-soluble lower alcohols.

The combined reaction and wash waters after the removal of the water-soluble alcohols by distillation, may still contain salts of fatty acids. These may be obtained in the dry state by evaporating the water. It is possible to react these dry salts by a treatment with a strong gaseous acid to form the sodium salts of these acids and raw fatty acids. The raw fatty acids will contain for the most part mineral acid requiring an after-treatment. This after-treatment is most conveniently effected by treating the mineral acid-containing raw fatty acids with dry salts of fatty acids in amount corresponding to the acid content in order to neutralize the acid.

The following example is given to illustrate the invention and not to limit the same:

EXAMPLE 1

9450 grams of reaction water, having a saponification number of 37, 7430 grams of cold condensate having a saponification number of 23, and 1116 grams of hot condensate having a saponification number of 9, i.e. a total of 17,996 grams of Oxyl products, together with 456 grams of chemically pure sodium hydroxide (120% of the saponification number) were placed into an autoclave of 30 liters capacity and heated to 200° C., while the mass was stirred. After having reached this temperature the stirrer was stopped. After 5 minutes, the aqueous-

alcoholic layer was drawn off through a filter candle. 8,630 cc. of an alcoholic-aqueous salt solution were obtained, upon which 160 cc. of water-insoluble alcohols were floating.

5           2 liters of hot water were then added to the auto-  
clave and stirred with the remaining oily layer for 15  
minutes at a temperature of 160 to 200° C. Then the  
aqueous portion was again drawn off through the filter  
candle, whereby 2260 cc. of soap solution were obtained.  
10 This second washing solution was combined with the  
alcoholic-aqueous soap solution drawn off at first.  
The oily layer remaining in the autoclave was filtered,  
and then subjected to a normal pressure distillation up  
to 200° C., whereupon the distillation was continued  
15 with the use of vacuum up to a temperature corresponding  
to 380° C. at 760 mm. 1085 grams of paraffin having  
the following characteristics were left as the residue  
from distillation boiling above 380° C.:

20	Neutralization number	0
	Ester number	0
	Hydroxyl number	20
	Iodine number	10
	Carbonyl number	3

25 The distillate obtained consisted of 5470 cc. of oily  
portions and 740 cc. of aqueous portions boiling up to  
200° C. and 2930 cc. of oily portions boiling between  
200 and 380° C. The characteristics of these portions  
were as follows:

	Neutraliza- tion No.	Ester No.	Hydroxyl No.	Iodine No.	Carbonyl No.	Density at 20°C.
below 200° C.:						
oily portions:	0	0	272	100	17	0.736
aqueous portions:	0	0	428	0	0	0.941
5 200 - 380° C.:	0	0	169	39	18	0.805

The distillates recovered were then formylated in the known manner by the catalytic addition of water gas in the presence of cobalt compounds and the formylation products were subjected to a hydrating hydrogenation with hydrogen in the presence of water. 8900 cc. corresponding to 7200 grams of formylation product were obtained, having the following characteristics:

	Neutralization number	0
	Ester number	1
15	Hydroxyl number	361
	Iodine number	1
	Carbonyl number	2
	Density at 20° C.	0.808

This product was continuously extracted in three stages with 42 liters of 70% ethanol at a ratio of 1 : 4. The temperature was approximately 35° C., the throughput was 500 cc. of raw alcohol per hour. 49.8 liters of extract and 0.834 liters of raffinate were obtained. The extract was distilled from a still without fractionating attachment at an overhead temperature of 85° C., whereby 25.9 liters of distillate were obtained. 21.55 liters of residue also consisting of two layers remained in the still. The upper layer consisted of 7.95 liters of alcohols having the following characteristics:



	Iodine number	1
	Neutralization number	1
	Ester number	1
	Hydroxyl number	492
5	Carbonyl number	2
	Density at 20° C.	0.833
	Refractive index, $n_D^{20}$	1.4140

The lower layer consisted of 13.6 liters of aqueous ethyl alcohol containing approximately 25% by volume of  $C_2H_5OH$ . This lower layer was combined with the 25.9 liters of distillate whereby a total of 0.740 liters was obtained as the upper oily layer which had the following characteristics:

	Neutralization number	0
15	Ester number	1.2
	Hydroxyl number	25
	Carbonyl number	2
	Density at 20° C.	0.727
	Refractive index, $n_D^{20}$	1.4105

It consisted of hydrocarbons having a slight content of ethyl alcohol. The lower layer consisted of approximately 39 liters of 70% ethyl alcohol which was charged to a new extraction. The raffinate consisting of 0.834 liters was distilled up to 105° C. in order to remove the ethanol contained therein, whereby 95 cc. of aqueous ethyl alcohol were obtained. Moreover, 62 cc. of gasoline distilled, which were returned into the raffinate. Thus, a total of 1234 grams of raffinate having a hydroxyl number of 34 were obtained. The feed stock consisted of 7200 grams and had a hydroxyl number of 361. Thus, the extraction effect was 98.4%.

The concentration of the charged raw alcohols was approximately 85%. The extracted alcohols could be separated by fractionation into alcohol cuts of a certain chain length.

5           The alcoholic-aqueous portion drawn off from the autoclave and the wash solution combined with this portion were distilled until an overhead temperature of 100° C. was reached and the remaining aqueous residue from distillation was evaporated to dryness.  
10       991 grams of dry salts were obtained thereby in which 859 grams of alkali compounds of lower fatty acids were contained. The balance of 132 grams consisted of soda originating from the alkali excess of the ester splitting. The dry salts of fatty acids were treated  
15       in a tube at 180° C. with a dry stream of hydrogen chloride whereby 700 grams of lower raw fatty acids were obtained, which were stirred with salts of fatty acids in amount of about 25% of their weight and separated by filtration from the sodium chloride  
20       formed.

          The paraffin remaining after the distillation of the oily layers was processed into commercial paraffins in the known manner by a treatment with hydrogen in the presence of a catalyst and, if necessary or  
25       desired, by a selective extraction.

THE embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the separation of alcohol hydrocarbon mixtures with the neutralization and splitting of the acids and esters present by saponification at an elevated temperature and an increased pressure sufficient to prevent evaporation of the components of the mixture, the improvement which comprises effecting the saponification with sodium hydroxide present in amount not in excess of 20% in excess of the theoretical required quantity based on the ester number and the neutralization number of the mixture, removing the precipitated metallic oxides, and separating the alkaline aqueous layer containing the water-soluble alcohols from the upper oily layer at said elevated saponification temperature.
2. Improvement according to Claim 1, in which said separation of the precipitated metal oxides is effected by filtration.
3. Improvement according to Claim 2, in which said filtration is effected under pressure.
4. Improvement according to Claim 1, in which said saponification is effected in the presence of at least one lower alcohol having 2 to 5 carbon atoms.
5. Improvement according to Claim 1, which includes the addition of at least one lower alcohol having 2 to 5 carbon atoms after said saponification.
6. Improvement according to Claim 1, in which said alcohol hydrocarbon mixtures are mixtures obtained from the catalytic hydrogenation of carbon monoxide including the reaction water and all of the condensation products, and which includes stirring said mixture into an emulsion with said sodium hydroxide for said saponification.

7. Improvement according to Claim 1, which includes washing said oily layer with preheated water under pressure at said saponification temperature.
8. Improvement according to Claim 7, which includes removing higher alcohols from said oily layer with water containing from about 30 to 50 parts of at least one water-soluble lower alcohol having from 1 to 5 carbon atoms at elevated temperature and pressure.
9. Improvement according to Claim 8, in which said oily layer is distilled at normal pressure and thereafter vacuum distilled, after said higher alcohol removal.
10. Improvement according to Claim 9, which includes washing said oily layer with pure water under pressure after said higher alcohol removal and before said distillation.
11. Improvement according to Claim 1, in which said oily layer is washed and which includes converting the olefins in the washed oily layers into alcohols by formylation and hydrogenation, and recovering the formed alcohols from saturated hydrocarbons.
12. Improvement according to Claim 11, which includes mildly hydrogenating insoluble raw alcohols separated from the hydrocarbons for the saturation thereof and conversion of any ketones into secondary alcohols.
13. Improvement according to Claim 12, which includes dissolving the mildly hydrogenated alcohols in alcohol water mixtures and distilling the alcohol water mixture for separation from the residual hydrocarbons.

14. Improvement according to claim 1, which includes cooling the alkaline aqueous layer for the formation of an upper and lower layer, separating the upper layer formed which contains the higher alcohols, and distilling the remaining combined alkaline wash and reaction waters for the recovery of water-soluble alcohols.

15. Improvement according to claim 14, which includes evaporating said combined alkaline wash and reaction waters after the distillation thereof, and recovering dry salts of fatty acids.

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