PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Separation of Oxygen-Containing Compounds from their Mixtures with Hydrocarbons

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, and LURGI GESELLSCHAFT FUR WARMETECHNIK M.B.H., of Frankfurt a.M., Heddernheim, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the separation of oxygen-containing compounds from their mixtures with hydrocarbons.

By the use of suitable synthesis conditions, primary products may be obtained in the catalytic hydrogenation of carbon monoxide, which contain larger quantities of alcohols, esters, aldehydes, acids and the like, than of hydrocarbons. In the processing of these mixtures, the esters present cause considerable difficulties because the separation of the alcohols from the hydrocarbon is considerably disturbed by the presence of the esters so that processes using selective extraction or azeotropic distillation can be carried out for this purpose only with difficulty. The splitting or saponification of the esters by treatment with caustic potash solution or caustic soda solution with the formation of salts of fatty acids and alcohols has been proposed for the processing of these mixtures. However, the use of the cheap caustic soda solution has been found to be disadvantageous because it leads to the formation of solid soaps which form emulsions, particularly with long-chain hydrocarbons, so that it is difficult to separate them from the reaction products.

Furthermore, the caustic alkali solutions used in the treatment of the mixture of synthetic products have hitherto been of relatively high concentration, with the result that losses have been increased through the occurrence of undesirable side-reactions, such as aldol condensations and resin formation.

It has also been proposed to carry out the saponification at elevated temperature and under a pressure sufficiently high to prevent vaporisation of the constituents of the mixture, whereupon the vaporizable constituents are distilled from the reaction mixture by releasing the pressure.

It is an object of the invention to provide a method for the processing of such mixtures with the use of sodium hydroxide, whereby the disadvantages involved in prior methods employing sodium hydroxide are avoided or considerably reduced.

According to the invention, the processing of alcohol-hydrocarbon mixtures, particularly such mixtures when obtained as the products of the caatlytic hydrogenation of carbon monoxide, by saponification of the esters and neutralization of the acids with sodium hydroxide at elevated temperature and under a pressure which is such that no vaporisation of the components of the mixture occurs, is effected by using a quantity of sodium hydroxide not higher than 20% in excess of the theoretically required quantity, based on the ester number and the neutralization number of the mixture, removing any precipitated metal oxides by filtration, the filtration being carried out, if necessary or desired, under pressure, and separating the aqueous alkaline layer containing the water-soluble alcohols from the upper hydrocarbon layer at the temperatures used in the saponification of the esters.

Metal oxides will generally be precipitated during the saponification when the alcohol-hydrocarbon mixture being treated is a product of the catalytic hydrogenation of carbon monoxide. Such metal oxides are derived from heavy metal compounds in solution in the mixture, the heavy metal compounds originating from the catalyst used in the synthesis of the mixture and/or from the metal of the synthesis reactor.

It has been found particularly advantageous to carry out the ester splitting with caustic soda solution in the presence of one or more lower alcohols containing from 2 to 5 carbon atoms in the molecule. During the saponification of the esters, the lower alcohols act as dissolving intermediaries between the aqueous caustic soda solution and the water-insoluble esters, that is to say, they promote the for-

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mation of an emulsion. After completion of the reaction, however, the lower alcohol of mixture of lower alcohols acts as a demulsifier or emulsion breaker, which action is desirable at that stage. For these reasons, their presence during and after the saponification is desirable so that one or more of the lower alcohols should be added, if necessary, to the mixture before saponification. It is advantageous, therefore, to operate in such a manner that the total alcohol-hydrocarbon mixture, including the reaction water produced in the hydrogenation of carbon monoxide, is stirred into an emulsion with a quantity of sodium hydroxide which does not exceed the quantity theoretically required for the saponification and neutralization by more than 20%, with, if required, the addition of one or more C_2—C_5 alcohols.

The processing of the hydrocarbon layer separated from the aqueous alkaline layer is preferably commenced by a washing with preheated water under pressure, carried out at the temperature of the saponification. This washing is suitably followed by a second washing carried out under the same conditions with water to which 30 to 50 parts by volume of one or more water-soluble lower alcohols of the molecular size C_1—C_3, for example, methyl alcohol, ethyl alcohol, propyl alcohol, and the like, have been added. If required, a final washing with pure water under pressure may follow. After this washing, the hydrocarbon layer may be subjected to distillation under normal pressure followed by vacuum distillation.

In order to increase the yield of alcohols, it is possible to subject any olefins present in the washed hydrocarbon layer, which is freed, if necessary or required, from solid paraffins or waxes to the Oxo synthesis. In this case, the olefins are converted into aldehydes in known manner by the catalytic addition of carbon monoxide and hydrogen at elevated pressure and elevated temperature, that is to say, the olefins are formylated. These aldehydes may then be converted into alcohols by hydrogenation.

The alcohols may be separated from the remaining saturated hydrocarbons in known manner, for example, by selective extraction or by azeotropic distillation.

The water-insoluble raw alcohols separated in the described manner from the hydrocarbons, may still contain 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 are converted into secondary alcohols.

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

The alkaline aqueous solution which separates and is drawn off as the lower layer from the upper hydrocarbon layer of the saponification product under the conditions described, is first cooled; this results in the formation of two layers. The newly formed upper layer, containing higher alcohols, is separated and the remaining layer containing the combined alkaline washing and reaction waters may be subjected to distillation for the recovery of the water-soluble lower alcohols.

The salts of fatty acids still present in the combined reaction and wash waters after having distilled off the water-soluble alcohols, may be obtained in the dry state by evaporation of the water. It is possible to treat them with strong gaseous acids to give sodium salts of these acids and crude fatty acids. However, these crude fatty acids generally contain mineral acid and require an after-treatment which is most conveniently carried out by treating the mineral acid-containing crude fatty acids with dry salts of fatty acids in an amount equivalent to the mineral acid content, in order to neutralize the acid.

The invention is illustrated by the following example:—

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, that is, a total of 17,996 grams of Oxyl product, together with 456 grams of chemically pure sodium hydroxide (120% of the saponification number) were placed in an autoclave of 30 litres capacity and heated to 200° C. with stirring. After the mixture had reached this temperature, the stirrer was stopped. After 5 minutes, the mixture had separated into an upper oily or hydrocarbon layer and a lower aqueous-alcoholic layer. The aqueous-alcoholic layer was drawn off through a filter candle, 8,630 cc. of an alcoholic-aqueous salt solution being obtained upon which 160 cc. of water-insoluble alcohols were floating.

2 litres of hot water were then introduced into the autoclave and stirred for 15 minutes at a temperature of from 160° C. to 200° C. with the hydrocarbon layer. The mixture was allowed to settle and the aqueous layer was drawn off through the filter candle, 2260 cc. of soap solution being obtained. This second washing solution was combined with the alcoholic aqueous soap solution first drawn off. The hydrocarbon layer remaining in the autoclave was filtered and then subjected to a normal pressure distillation up to 200° C., whereupon the distillation was continued under reduced pressure up to a temperature corresponding to 380° C. at 760 mm. 1,085 grams of solid hydrocarbons boiling above 380° C.

and having the following characteristics remained as the residue of the distillation:—

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

The distillate obtained consisted of 5470 cc. of a hydrocarbon fraction and 740 cc. of an aqueous fraction, both fractions boiling up to 200° C., and 2930 cc. of a hydrocarbon fraction boiling between 200° C. and 380° C. The characteristics of these fractions were as follows:—

	Neutralization number	Ester number	Hydroxyl number	Iodine number	Carbonyl number	Density at 20° C.
Below 200° C.:—						
hydrocarbon fraction	0	0	272	100	17	0.736
aqueous fraction	0	0	428	0	0	0.941
200° C.—380° C.	0	0	169	39	18	0.805

The hydrocarbon distillate fractions recovered were then formylated in known manner by the catalytic addition of water gas in the presence of a cobalt compound and the formylation products were subjected to a hydrating hydrogenation with hydrogen in the presence of water. 8,900 cc. corresponding to 7,200 grams of formylation product were obtained having the following characteristics:—

Neutralization number	0
Ester number	1
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 litres 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 litres of extract and 0.834 litres of raffinite were obtained. The extract was distilled in a still, without a fractionating column, at an overhead temperature of 85° C., whereby 25.9 litres of distillate were obtained. 21.55 litres of residue, which separated into two layers, remained in the still. The upper layer consisted of 7.95 litres of alcohols having the following characteristics:—

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

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

Neutralization number	0
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 litres of 70% ethyl alcohol which was charged to a new extraction. The raffinate consisting of 0.834 litres was distilled up to 105° C. in order to remove the ethyl alcohol contained therein, whereby 95 cc. of aqueous ethyl alcohol were obtained. Moreover, 62 cc. of hydrocarbons boiling in the gasoline range distilled over which were returned to the raffinate. Thus a total of 1234 grams of raffinate having a hydroxyl number of 34 were obtained. The feedstock 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 determined chain length.

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

The solid hydrocarbon remaining after the distillation of the hydrocarbon layers was processed into commercial paraffin waxes in known manner by treatment with hydrogen in the presence of a catalyst and, where necessary or desired, by selective extraction.

What we claim is:—

1. A process for the neutralization and

saponification of the acids and esters present in alcohol-hydrocarbon mixtures, particularly such mixtures obtained in the catalytic hydrogenation of carbon monoxide, by treatment with sodium hydroxide at elevated temperature and at a pressure at which substantially no evaporation of the components of the mixture occurs, which comprises using a quantity of sodium hydroxide not higher than 20% in excess of the theoretically required quantity, based on the ester number and the neutralization number of the mixture, removing any precipitated metal oxides by filtration, and separating the alkaline aqueous layer with the water-soluble alcohols from the upper hydrocarbon layer at the temperatures used in the ester saponification.

2. A process according to claim 1, in which the neutralization and saponification is carried out in the presence of one or more C_2—C_5 alcohols to emulsify the sodium hydroxide and water-insoluble esters during the saponification.

3. A process according to claim 1 or claim 2, in which the total alcohol-hydrocarbon mixture including the reaction water obtained in the hydrogenation of carbon monoxide and including all of the condensation products are stirred into an emulsion with the sodium hydroxide used for the saponification and neutralization, with the addition, if necessary, or desired of C_2—C_5 alcohols.

4. A process according to any one of the preceding claims, in which the hydrocarbon layer is washed with preheated water under pressure at the temperature of the ester saponification, prior to being subjected to further treatment.

5. A process according to any one of the preceding claims, in which the hydrocarbon layer is freed from higher alcohols in known manner under pressure and at elevated temperature by means of water to which 30 to 50 parts by volume of one or more water-soluble C_1—C_5 alcohols have been added, whereupon, if necessary or desired, a final washing with pure water under pressure is effected.

6. A process according to any one of the preceding claims, in which the hydrocarbon layer is subjected to distillation under normal pressure and subsequently to vacuum distillation.

7. A process according to any one of claims 4 to 6, in which any olefins present in the washed hydrocarbon layer which, if necessary or desired, has been freed from solid hydrocarbons, are converted into alcohols in known manner by formylation and hydrogenation, and the alcohols recovered are separated in known manner from the saturated hydrocarbons.

8. A process according to claim 7, in which the water-insoluble raw alcohols separated from the hydrocarbons are subjected to hydrogenation under mild conditions in order to convert unsaturated alcohols into saturated alcohols and ketones into secondary alcohols.

9. A process according to claim 8, in which the mildly hydrogenated alcohols are, for the purpose of removing any hydrocarbons still present in small amounts, dissolved in alcohol-water mixtures and are freed from the residual hydrocarbons by separating a part of the alcohol-water mixture by distillation.

10. A process according to any one of claims 1 to 3, which includes cooling the alkaline aqueous layer, separating the upper layer formed thereby and containing higher alcohols, and subjecting the remaining combined alkaline wash and reaction waters to distillation for the recovery of the water-insoluble alcohols.

11. A process according to claim 10, in which the salts of fatty acids still present in the combined alkaline reaction and wash waters after distilling off the water-soluble alcohols, are recovered in the dry state by evaporating the water.

12. A process according to claims 1, 2, 3, 10 or 11, in which the salts of fatty acids obtained in accordance with claim 4 are reacted with a strong acid in the gaseous state, for example, hydrogen chloride.

13. A process according to claim 12, in which the acid-containing crude fatty acids recovered are treated, for the purpose of neutralizing mineral acid, with dry fatty acid salts in amount equivalent to the mineral acid content.

14. A process according to any one of the preceding claims, in which the filtration for the removal of precipitated metal oxides is carried out under pressure.

15. A process for the separation of oxygen-containing compounds from their mixtures with hydrocarbons, substantially as hereinbefore described with reference to the example.

16. A process for the treatment of alcohol-hydrocarbon mixtures obtained as products of the hydrogenation of carbon monoxide, substantially as hereinbefore described.

17. A process for the treatment of mixtures of alcohols, esters, aldehydes, fatty acids and hydrocarbons, substantially as hereinbefore described.

18. Alcohols, fatty acids and hydrocarbons, whenever separated and obtained by the process of any preceding claim.

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ERRATA

SPECIFICATION NO. 736,404

Page 1, line 60, *for* "caatlytic" *read* "catalytic".
Page 2, line 86, *for* "creede" *read* "crude".
Page 3, line 42, *for* "raffinite" *read* "raffinate".
Page 3, line 72, *for* "lleyer" *read* "layer".
Page 3, line 102, *for* "steam" *read* "stream".

THE PATENT OFFICE,
10th October, 1955

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We, RUHRCHEMIE AKTIENGESELLSCHAFT, of

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