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RECOVERY OF ORGANIC ACIDS FROM OXIDATION PRODUCTS OF HYDROCARBONS

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The present invention relates to improvements in the recovery of organic acids from products of the oxidation of liquid and solid, non-aromatic hydrocarbons.

In the oxidation of liquid or solid, non-aromatic i. e. open chain aliphatic or cycloaliphatic hydrocarbons, such as scale wax, purified paraffin wax, paraffin oils, cracked fractions of petrolatum, cracked or hydrogenated mineral oils or mineral oil fractions, in the liquid-phase with air or other oxidizing agents, such as nitrogen oxides, oxygen etc., a mixture of oxygen-containing products and unattacked starting material is usually obtained.

The oxygen-containing compounds can be divided into two groups, namely the saponifiable part and the unsaponifiable part. It is especially the saponifiable part with which we are here concerned. The components thereof belong to many different groups of organic compounds; besides ordinary carboxylic acids such as fatty acids and their esters, derivatives thereof such as hydroxy acids, ester acids, aldehyde- and keto acids or lactones, estalides, lactides, etc. are present in greater or less amounts. These derivatives exert a considerable influence on the peculiar properties of the saponifiable part of the oxidation products from the above mentioned hydrocarbons.

The saponifiable parts of the raw oxidation products, when free from true esters, still show a difference between acid- and saponification number; this difference is attributed to the presence in the said saponifiable products of such complicated oxygen-containing compounds as lactones, lactides, ester acids and perhaps true acid anhydrides.

The above mentioned derivatives, especially hydroxy acids and lactones, injure quite considerably the quality of the ordinary acid oxidation products, such as the saturated carboxylic acids. Their obnoxiousness is especially noticeable in the use of the ordinary carboxylic acids for the soap industry where they cause discoloration of the soap and difficulties in the preparation of the soap. Up to the present time, the said undesired derivatives could be separated from the normal acid products only by expensive methods.

As a very surprising fact we have now found that ordinary carboxylic acids in the free state or in the form of their salts can be obtained in increased yields free from the said undesirable by-products and in a state very suitable for various technical purposes by subjecting the oxidation products as a whole or fractions thereof to a treatment with hydrogen in the presence of an alkaline reacting agent under increased pressure; thereby the injurious parts of the oxidation products are reduced to ordinary carboxylic acids or hydrocarbons, while the ordinary carboxylic acids are practically not attacked.

It appears that by working in the presence of an alkaline reacting agent, only the lactonic ring systems, ester acids or other condensation products, but not the normal carboxylic acids are brought into a structural state where they are accessible to hydrogenation under the conditions set forth below, so that a selective hydrogenation can be carried out which is not possible in the absence of an alkaline reacting agent.

To carry the present method into practice, the entire oxidation products of liquid or solid, non-aromatic hydrocarbons, as above referred to, or fractions thereof, obtained by any suitable method, for example by distillation or extraction, are treated with hydrogen in the presence of alkaline reacting agents, such as oxides, hydroxides or carbonates of the alkalies or alkaline earth metals, or of organic bases, at temperatures of from about 150° to about 300° C. A preferred temperature is about 300° C.

Pressures of hydrogen of from 10 to 300 atmospheres may be applied; however, for practical reasons one will usually work below the upper limit, for instance, between 50 and 200 atmospheres. Usually the reaction is finished after a short time.

The presence of hydrogenation catalysts, for example of such as comprise copper, nickel, cobalt or the like may be advantageous, although it is not absolutely necessary in order to secure completion of the reaction; the catalysts can be applied, for instance, in the form of their oxides, hydroxides, or carbonates, or also as free metals in finely divided form; they may also be employed on carrier substances such as diatomaceous earth.

Ordinarily the purity of the hydrogen used is without significance; the presence of inert gases or of carbon monoxide does not disturb the reaction.

If desired, the oxidation products can be submitted to the treatment, dissolved in suitable organic solvents such as hydrocarbons.

The addition of the alkaline agents to the oxidation products and their action thereon can take place before or simultaneously with the hydrogenation treatment. The alkaline agents can be applied in dry form, or dissolved or suspended in water; it is advantageous for the better execution of the reaction to remove from the reaction mixture, as completely as possible before the reaction is finished, the water present from the aqueous solution of the alkaline agent and/or the water resulting from the saponification. If high temperatures are used in the saponification, the reaction should be started in an atmosphere of hydrogen in order to exclude undesirable side-reactions. The amount of the alkaline agent is

suitably determined on the basis of the saponification number of the product to be treated; generally one will work with an excess of the saponification agent; however, the reaction is also feasible when a smaller amount than that theoretically required is used. If the free acids are to be produced the soap solutions obtained are acidified in the usual manner and the acids recovered.

The reaction is carried out in a pressure vessel which is provided with a high-speed stirrer or any other device which permits intimately mixing the saponified oxidation products with the hydrogen. Unsaponifiable constituents present in the materials to be treated do not exert an undesired effect; on the contrary the unsaponifiable constituents act as solvents or diluents for the liquid anhydrous soaps and thus help to avoid a cracking of the soaps at the high temperatures employed.

After the hydrogenation treatment, the oxidation product is worked up in any suitable manner; the unsaponifiable parts, such as aldehydes, ketones, alcohols and unchanged hydrocarbons are removed from the soaps by extraction with low boiling hydrocarbons or by distillation, whereupon the soap may be decomposed with mineral acids. The fatty acids thus obtainable are preferably submitted to another distillation before being used in the soap industry. For many purposes, however, they are applicable without further distillation.

The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples. The parts are by weight.

Example 1

500 parts of an oxidation product, obtained by oxidation in the liquid phase of crude scale wax with air at about 140° C. and containing 44 per cent of unsaponifiable components, are treated with an amount of anhydrous caustic soda 4 per cent in excess of that required for a complete saponification of the fatty acids and the esters, with the addition of 25 parts of a nickel-kieselguhr catalyst which has been reduced at 450° C., and which contains 20 per cent of nickel, for two hours while stirring, at from 290° to 300° C. in an autoclave. During this procedure, the water produced by the saponification was removed at 250° C. and 300° C. respectively, by releasing the pressure prevailing in the autoclave; after each release, a pressure of 10 atmospheres of hydrogen was put upon the autoclave and finally, when a temperature of 300° C. was reached, the hydrogen pressure was increased to 50 atmospheres.

After cooling the reaction mass is treated with water. The unsaponifiable components are removed by extraction with low boiling hydrocarbons, and then from the aqueous soap solution the fatty acids were liberated by means of diluted sulphuric acid.

After washing with water, these fatty acids show the following analytical values:

Acid number	199
Saponification number	208
Ester number	9
Per cent hydroxy acids	0.6

The color of these fatty acids is light brown.

When the saponification is carried out in the absence of hydrogen and catalysts, dark brown fatty acids are obtained with ester numbers of from 35 to 70 and with from 8 to 15 per cent of hydroxy acids.

Example 2

500 parts of an oxidation product, obtained by oxidation of crude scale wax with air, in the liquid phase, and containing 56 per cent of unsaponifiable components, are washed with water for the removal of water-soluble acids and saponified with 95 per cent of the amount of potassium hydroxide necessary for the complete saponification. The mixture obtained is treated with the addition of 50 parts of basic copper carbonate, for a period of two hours at from about 290° to 300° C. in an autoclave provided with a stirrer. On heating up the reaction mixture, a pressure of 10 atmospheres of hydrogen was supplied, and on reaching a temperature of 300° C., the pressure was increased to 50 atmospheres of hydrogen.

According to the working-up method of Example 1, very light colored fatty acids are obtained from the reaction mixture, which possesses an acid number of 190, saponification number of 206, ester number of 16, and 1.5 per cent of hydroxy acids. The fatty acids obtained from the same oxidation product by saponification without the catalytic treatment with hydrogen possess an ester number of 35, and contain 9 per cent of hydroxy acids.

Example 3

500 parts of the oxidation product referred to in Example 2, are saponified with an excess of dry caustic soda, under a pressure of 50 atmospheres of hydrogen, at from 290° to 300° C., and in the absence of a catalyst. The ester number of the fatty acids liberated in accordance with the procedure in Example 1 amounts to 13, the content in hydroxy acids to 3 per cent; in a reaction product from the same starting material, but saponified in the absence of hydrogen, an ester number of 30, and 12.5 per cent of hydroxy acids were found.

Example 4

500 parts of the oxidation product referred to in Example 2 are treated with an amount of calcium hydroxide which is 7.5 per cent in excess of the amount theoretically necessary for the complete saponification of the fatty acids and esters, with the addition of 20 parts of basic copper carbonate while stirring for 2 hours at about 300° C. in an autoclave. The water formed in the saponification is removed and the treatment with hydrogen is carried out in the manner described in Example 1.

The reaction mixture obtained is allowed to cool, disintegrated mechanically and heated to boiling with an excess of aqueous sodium carbonate solution until the calcium soaps have been converted into the sodium soaps. After removal of the calcium carbonate precipitated the filtrate is worked up as described in Example 1. The crude mixture of fatty acids obtained has the following characteristics after washing:

Acid number	195
Saponification number	207
Ester number	12
Per cent hydroxy acids	1.6

The crude fatty acid mixture is subjected to a steam-distillation under a pressure of from 10 to 15 millimeters, the maximum temperature being about 280° C. The characteristics of the fatty acid mixture thus obtained are as follows:

Acid number	212
Saponification number	215
Ester number	3
Per cent hydroxy acids	0

The color of the product determined in the 6''-cell of the Lovibond-tintometer is: yellow 25 and red 4.5 (see "Holde, Kahlenwassertöffale und Fette", 7th ed., 1933, pages 233/34).

A crude fatty acid mixture obtained from the same oxidation product by saponification at about 150° C. in the absence of hydrogen and of catalysts and by extraction according to Example 1 yields by steam-distillation in vacuo a fatty acid mixture of the following characteristics:

Acid number	195
Saponification number	249
Ester number	54

Color (determined as above): yellow 45 and red 23

Example 5

500 parts of the oxidation product referred to in Example 2 are saponified with anhydrous sodium carbonate (which is employed in an excess of 10 per cent of the amount theoretically necessary for the complete saponification of the fatty acids and esters) with the addition of 40 parts of cupric sulphate ($CuSO_4.5H_2O$) for 2 hours at from 290° to 300° C. in a stirring autoclave. The removal of the water formed in the saponification is carried out in an analogous manner as described in Example 1, with the only difference that the hydrogen pressure applied after releasing the autoclave is 100 atmospheres and, after the temperature of 300° C. has been reached, 200 atmospheres.

If the reaction mixture is worked up as described in Example 1, after the steam-distillation in vacuo a fatty acid mixture is obtained which has the following characteristics:

Acid number	227
Saponification number	227
Ester number	0
Per cent hydroxy acids	0

Color (determined as indicated in Example 4) yellow 30 and red 8.5

Example 6

1 part of zinc dust is mixed with 10 parts of a hot saturated cupric sulphate solution; if the reaction is completed, the mixture is evaporated to dryness. 500 parts of the oxidation product referred to in Example 2 are treated with the catalyst thus obtained and anhydrous sodium carbonate (in an excess of 10 per cent of the amount theoretically necessary for saponifying the fatty acids and esters) for 2 hours at from 290° to 300° C. in a stirring autoclave. The removal of the water formed during the saponification, the treatment with hydrogen and the working up of the reaction mixture is carried out as described in Example 1.

A fatty acid mixture is thus obtained which after steam-distillation under the conditions indicated in Example 4 possesses the following characteristics:

Acid number	217
Saponification number	221
Ester number	4
Per cent hydroxy acids	0

Color (determined as indicated in Example 4) yellow 4 and red 7

Example 7

500 parts of the oxidation product referred to in Example 2 are treated in a stirring autoclave for 2 hours at about 300° C. with anhydrous sodium carbonate (10 per cent excess of the amount theoretically necessary for the complete saponification of the fatty acids and esters) with an addition of 5 parts of zinc dust. The removal of the water formed in the saponification is carried out as indicated in Example 1 and the treatment with hydrogen is effected in the manner described in Example 5.

After working up the reaction mixture as described in Example 1 a fatty acid mixture is obtained which after steam-distillation in vacuo has the following characteristics:

Acid number	226
Saponification number	228
Ester number	2
Per cent hydroxy acids	0

Color (determined as indicated in Example 4) yellow 30 and red 10

By means of the hydrogenation in an alkaline medium disclosed in the above examples generally raw fatty acids are obtained which are substantially lighter colored than those obtained by the usual saponification without hydrogen. A further, very substantial advantage of the present method consists in a noticeable increase of the yield in raw fatty acids, which is due to the prevention of condensation and polymerization reactions on account of the influence of the hydrogen.

What we claim is:

1. A process for recovering fatty acids which comprises subjecting an oxidation product from the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, comprising the saponifiable constituents formed in the oxidation, to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent.

2. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent and separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part.

3. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent, separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part and setting free the acids from the latter.

4. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the saponifiable part of the oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent.

5. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the saponifiable part of the oxidation

product to a hydrogenation treatment under super-atmospheric pressure in the presence of an alkaline reacting agent and setting free the acids from the latter.

6. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali and alkaline earth metals and of organic bases and separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part.

7. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent the amount of which corresponds substantially to the saponification number of the entire oxidation product, separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part.

8. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment in the presence of an alkaline reacting agent at temperatures of from about 150° C. to about 350° C. and under a pressure from about 10 to about 300 atmospheres of hydrogen and separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part.

9. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment in the presence of an alkaline reacting agent at temperatures of from about 150° C. to about 350° C. and under a pressure from about 10 to about 300 atmospheres of hydrogen, separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part and setting free the acids from the latter.

10. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting, substantially water-free agent, care being taken that any water produced by the reaction is removed from the mixture while the hydrogenation is still in progress and separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part.

11. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent and in the presence of a hydrogenating catalyst, and separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part.

12. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of crude scale wax, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent and separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part.

13. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of crude scale wax, in the form of fatty acids, which comprises subjecting the entire oxidation product to a hydrogenation treatment under superatmospheric pressure in the presence of an alkaline reacting agent, the amount of which corresponds substantially to the saponification number of the entire oxidation product, separating the unsaponifiable part of the oxidation product from the saponified hydrogenated part and setting free the acids from the latter.

14. A process for recovering substantially the entire saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of crude scale wax, in the form of fatty acids, which comprises subjecting the entire oxidation product to a saponification treatment with an amount of caustic soda by 4 per cent in excess of that required for a complete saponification of the fatty acids and the esters present in the oxidation product, at temperatures of from 200° to 300° C. in an autoclave, care being taken that the water produced by the saponification is removed at 250° C. and 300° C., respectively, by releasing the pressure prevailing in the autoclave, and putting a pressure of 10 atmospheres of hydrogen upon the autoclave after each release, and increasing the hydrogen pressure when a temperature of 300° C. is reached, to 50 atmospheres, cooling the reaction mass, treating it with water, removing the unsaponifiable components by extraction with low-boiling hydrocarbons, and then decomposing the aqueous soap solution by means of a mineral acid.

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