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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 oxidation products of liquid or solid, non-aromatic hydrocarbons, such as scale wax, purified paraffin wax, paraffin oils, or cracked fractions of petrolatum.

In Patent No. 1,931,859, dated October 24th, 1933, one of us has described a process for the recovery of organic acids form the oxidation products of non-aromatic hydrocarbons, which is based on the saponification of the oxidation products with aqueous solutions of carbonates of the alkali metals or alkaline earth metals. It has also been proposed to saponify the oxidation products of non-aromatic hydrocarbons with oxides or hydroxides of the alkali metals or alkaline earth metals in order to recover the acid components.

As is known, the oxidation with air or other agents yielding oxygen, such as nitrogen oxides in the liquid or gaseous phase, yields besides the valuable normal carboxylic acids also hydroxy carboxylic acids or derivatives thereof, such as lactones, lactides, estolides, etc., which compounds we may designate as super-oxidized components of the oxidation products; they injure considerably the quality of the oxidation products.

By means of the known saponification methods, these undesirable super-oxidized components are obtained together with the carboxylic acids and can be removed therefrom only in a costly and complicated manner. The presence of these components can be recognized by the fact that the carboxylic acids are not completely soluble in low-boiling hydrocarbons on account of the presence, for instance, of hydroxy acids, and that the acid and saponification numbers of the acid parts which have been completely freed from unsaponifiable components, show a substantial difference which is usually designated as ester number.

Typical carboxylic acids as obtainable, for instance, by the oxidation of crude scale wax with air in the liquid phase, show an ester number of about 30 to 70 and a content of acids insoluble in low-boiling hydrocarbons, for instance, petrol ether, of about 5 to 15 per cent; these acids are hydroxy fatty acids.

We have now found that fatty acids free or practically free from the said undesired components such as hydroxy acids can be obtained from the oxidation products of from liquid to solid, non-aromatic i. e. open chain aliphatic or cycloaliphatic hydrocarbons by removing the water during the saponification which is carried out with alkaline reacting agents such as, for instance oxides, hydroxides, or carbonates of alkali or alkaline earth metals. Thus during the whole saponification period or at least a substantial part thereof, practically no water is present. The reaction can be commenced in the presence of water, but on reaching higher temperatures, great care must be taken that all the water, that is, the water which may have been used for dissolving or dispersing the alkaline reacting agent, and the water formed during the saponification reaction, is removed. Suitable temperatures are those of about 150° C. to about 300° C. For practical reasons one will work at about 280° to 300° C., whereby the reaction is usually finished in about 1 to 2 hours.

The presence of inert gases does not disturb the reaction; it may even be advantageous, yielding lightly colored products. Also, additions can be made which favor the splitting off of water or yield especially lightly colored products such as, for instance, aluminum oxide or metal powders of, for instance, zinc, copper, magnesium or aluminium.

While it is possible to work under ordinary pressure, reduced pressure may be applied whereby the removal of water from the highly heated soap is favored. On the other hand it may be of advantage to effect the saponification under increased pressure. The unsaponifiable parts present during the saponification of the saponifiable parts act presumably as solvents or diluents for the latter and thereby help to avoid undesired cracking of the soaps at the high temperatures applied. Unsaponifiable matter from an external source may be added to the material to be saponified for the same purpose.

The saponification can be carried out, for instance, with caustic alkalies, alkali carbonates, oxides or hydroxides of the alkaline earth metals or with mixtures of these alkaline reacting agents which may be employed in dry form or in aqueous solution or suspension, whereby generally an excess of about 3 to 8 per cent over the amount of saponifying agent, theoretically required, is applied; the theoretical amount is to correspond to the saponification number of the respective oxidation product. It may, however, be advantageous to employ lower amounts of the alkaline reacting reagents than the theoretical amount, for example 80 per cent of the latter.

Suitably, the reaction is carried through in a closed and heatable vessel provided with a stirrer, from which vessel the water vapor produced during the reaction, partly by the saponification reaction at 100° to 200° C., and partly by the splitting off of water from hydroxy acids or derivatives thereof at 180° to 350° C., is continuously released. The hydroxy acids are by this treatment, practically almost completely, transformed into other products, and the ester number of the oxidation product is substantially diminished or even disappears completely. Instead of continuously releasing the pressure it may be released from time to time.

If free acids are to be produced the saponification mixture is acidified and the acids are recovered. Otherwise the acids are obtained in the form of their salts.

The following table shows the results which were obtained in the saponification of the oxidation product of crude scale wax at low temperature in the presence of water, at high temperature in the presence of water and under pressure, and at high temperature in the absence of water. These results show clearly that the effect arrived at by saponification at a high temperature in the presence of water is considerably improved by working in the absence of water.

Analytical data of the fatty acids

Test number	Saponifying agent	Saponific. at 100–150° C., with water	Saponific. at 300° C., with water	Saponific. at 300° C., without water
1	NaOH	Ester number 30	20	9
		Per cent hydroxy acids 12.3.	5.6	0.9
2	NaOH hydrogen.	Ester number 30	26	7
		Per cent hydroxy acids 12.3.	1.9	0.5
3	Na_2CO_3	Ester number 54	28	0
		Per cent hydroxy acids 10.2.	2.3	0.8

The complete removal of the ester number is especially desirable.

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

Example 1

An oxidation product, obtained by oxidation of crude scale wax with air at 140° C. in the liquid phase and containing 44 per cent of unsaponifiable components, is washed with water for the removal of water-soluble acids, and thereupon saponified in an autoclave provided with a stirrer, with an amount of anhydrous caustic soda by 4 per cent in excess of the amount required for the complete saponification of the fatty acids and esters, for four hours and at from 290° to 300° C. After a temperature of 150° C. had been reached, the water produced by the saponification reaction is removed by releasing the pressure each time when the pressure in the autoclave had risen to about 10 atmospheres. The reaction is brought to a finish without the application of super-atmospheric pressure.

After cooling, the reaction mass is mixed with water and the unsaponifiable parts are removed by extraction with low-boiling hydrocarbons, and from the aqueous solution of the soaps the fatty acids are liberated by acidification with diluted sulphuric acid. After washing with water, these acids show the following analytical data:

Acid number	190
Saponification number	199
Ester number	9
Per cent hydroxy acids	0.9

Example 2

An oxidation product from purified scale wax containing 59 per cent of unsaponifiable components and obtained by oxidation with air at 140° C., in the presence of a manganese catalyst, is saponified with dry sodium carbonate in excess, at 290–300° C. in an autoclave provided with a stirrer, the pressure produced being released in the same manner as in Example 1. The reaction is brought to a finish in the absence of water and without the application of super-atmospheric pressure.

On application of the working-up method described in Example 1, fatty acids are obtained from the reaction mixture which, after distillation, show the following analytical data:

Acid number	240
Saponification number	240
Ester number	0
Per cent hydroxy acids	0

Example 3

The oxidation product referred to in Example 1 is mixed with a suspension of calcium hydroxide in 10 times its amount of water, calcium hydroxide being employed in an excess of 7.5 per cent of the amount theoretically necessary for the complete saponification of the fatty acids and esters. The mixture is treated for 2 hours in a stirring autoclave at from 290° to 300° C. The removal of the water added and formed during the saponification is effected by releasing the pressure after the temperature of 300° C. has been attained. The saponification is then completed without the application of super-atmospheric pressure. The saponification product obtained is mechanically disintegrated and heated to boiling with an excess of an aqueous sodium carbonate solution until the calcium soaps are converted into sodium soaps. After filtering off the calcium carbonate precipitated the filtrate is worked up in the manner described in Example 1. The crude fatty acid mixture thus obtained has the following characteristics:

Acid number	187
Saponification number	200
Ester number	13
Per cent hydroxy acids	2.4

This mixture is subjected to a steam-distillation under a pressure of from 10 to 15 millimeters mercury gauge with a maximum temperature of 280° C. The fatty acids thus obtained have the following characteristics:

Acid number	236
Saponification number	239
Ester number	3
Per cent hydroxy acids	0

The color of the product determined in the 6''-cell of the Lovibond-tintometer (compare "Holde, Kohlenwasserstoffe, Öle und Frette" 7th edition, 1933, pages 233 to 234) is yellow 40 and red 12.

Example 4

The oxidation product referred to in Example 1 is saponified with barium hydroxide

$(Ba(OH)_2.H_2O)$

under otherwise the same conditions as indicated in Example 3. After the steam-distillation in vacuo a fatty acid mixture is obtained which has the following characteristics:

Acid number	209
Saponification number	211
Ester number	2
Per cent hydroxy acids	0
Color (determined as indicated in Example 3)	yellow 35 and red 17.

Example 5

The oxidation product referred to in Example 2 is treated with anhydrous sodium carbonate

(85 per cent of the amount theoretically necessary for the complete saponification of the fatty acids and esters) for 2 hours at about 300° C. in a stirring autoclave, the water formed in the saponification being removed from the reaction mixture by temporarily releasing the pressure after a temperature of 300° C. has been attained.

After working up as described in Example 1 a crude fatty acid mixture is obtained which has the following characteristics:

Acid number	197
Saponification number	209
Ester number	12
Per cent hydroxy acids	1.9

After steam-distilling the product under the conditions stated in Example 3 a fatty acid mixture is obtained having the following characteristics:

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

Color (determined as indicated in Example 3) yellow 42 and red 7.5.

Example 6

The oxidation product referred to in Example 2 is treated for 2 hours at 300° C. with a 20 per cent aqueous solution of sodium carbonate which is employed in a 10 per cent excess of the amount theoretically necessary for completely saponifying the fatty acids and esters. The saponification is carried out under a pressure of from 25 to 40 millimeters mercury gauge in a vessel provided with a stirrer and a reflux-condenser which is heated with steam. The non-saponifiable compounds boiling above 100° C. are thus condensed and flow back into the reaction vessel while the water added and formed in the reaction distils off through the reflux condenser and is collected in a cooled receptacle.

After working up as described in Example 1 a mixture of fatty acids is obtained which after steam-distillation under the conditions of Example 3 has the following properties:

Acid number	223
Saponification number	223
Ester number	0
Per cent hydroxy acids	0

Color (determined as indicated in Example 3) yellow 30 and red 14.

Example 7

100 parts of the oxidation product referred to in Example 1 are treated with anhydrous sodium carbonate (10 per cent excess of the amount theoretically necessary for the complete saponification of the fatty acids and esters) with the addition of 75 parts of crude paraffin wax at about 300° C. for 2 hours in a stirring autoclave. As soon as the temperature of 300° C. is attained the water formed in the saponification is removed by release of the pressure and the saponification is completed under ordinary pressure.

The crude fatty acid mixture obtained by working up in the manner described in Example 1 has the following characteristics:

Acid number	193
Saponification number	204
Ester number	11
Per cent hydroxy acids	2.4

The fatty acids obtained by steam-distillation in vacuo of the said crude mixture have the following properties:

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

Color (determined as indicated in Example 3) yellow 24 and red 16.

Example 8

500 parts of the oxidation product referred to in Example 1 are treated for 2 hours at about 300° C. in a stirring autoclave with an amount of a 20 per cent aqueous sodium carbonate solution surpassing by 10 per cent the amount theoretically necessary for completely saponifying the fatty acids and esters, with the addition of 1 part of zinc dust. The water added and formed in the saponification is removed as described in Example 3.

The crude fatty acid mixture obtained by working up as indicated in Example 1 has the following characteristics:

Acid number	184
Saponification number	199
Ester number	15
Per cent hydroxy acids	0.8

By subjecting the crude mixture to a steam-distillation in the vacuum as described in Example 3 fatty acids are obtained which possess the following characteristics:

Acid number	245
Saponification number	245
Ester number	0
Per cent hydroxy acids	0

Color (determined as indicated in Example 3) yellow 30 and red 12.

If instead of the zinc dust 0.5 part of aluminium dust is employed a crude fatty acid mixture of the following characteristics is obtained:

Acid number	187
Saponification number	197
Ester number	10
Per cent hydroxy acids	1.5

By steam-distillation in vacuo this product yields a fatty acid mixture of the following characteristics:

Acid number	231
Saponification number	235
Ester number	4
Per cent hydroxy acids	0

Color (determined as indicated in Example 3) yellow 20 and red 10.

If instead of zinc dust 0.5 part of magnesium powder is added a fatty acid mixture is obtained which has the following characteristics:

Acid number	188
Saponification number	200
Ester number	12
Per cent hydroxy acids	1.8

After distilling the product as indicated above a fatty acid mixture of the following characteristics is obtained.

Acid number	242
Saponification number	245
Ester number	3

Per cent hydroxy acids..... 0
Color (determined as indicated in Example 3) yellow 24 and red 6.5.

Example 9

500 parts of the oxidation product referred to in Example 1 are treated in a stirring autoclave for 2 hours at about 300° C. with sodium hydroxide (40 per cent excess of the amount theoretically necessary for the complete saponification of the fatty acids and esters) with the addition of 25 parts of titanium dioxide. The water formed is removed as described in Example 5.

By working up as indicated in Example 1 a crude fatty acid mixture is obtained having the following characteristics:

Acid number	196
Saponification number	206
Ester number	10
Per cent hydroxy acids	2.3

After distilling this mixture in the manner indicated in Example 3 a fatty acid mixture of the following characteristics is obtained.

Acid number	227
Saponification number	232
Ester number	5
Per cent hydroxy acids	0
Color (determined as indicated in Example 3)	yellow 40 and red 10.5.

Example 10

The oxidation product referred to in Example 1 is admixed with anhydrous sodium carbonate which is employed in an excess of the amount theoretically necessary for the complete saponification of the fatty acids and esters; the mixture is heated under a hydrogen-pressure of 10 atmospheres; if the temperature of 150°, 200°, 250° and 300° C. are attained the pressure prevailing in the autoclave is released and fresh hydrogen is pressed in at the first three temperatures mentioned up to a pressure of 10 atmospheres and at 300° C. up to 50 atmospheres. The mixture is kept at 300° C. for 2 hours, after each 30 minutes the pressure being released and fresh hydrogen being pressed in up to a pressure of 50 atmospheres.

The crude fatty acid mixture obtained after working up as described in Example 1 has the following characteristics.

Acid number	169
Saponification number	182
Ester number	13
Per cent hydroxy acids	1.7

After distilling this product as described in Example 3 a fatty acid mixture is obtained which has the following characteristics.

Acid number	239
Saponification number	243
Ester number	4
Per cent hydroxy acids	0
Color (determined as indicated in Example 3)	yellow 30 and red 4.5.

What we claim is:

1. 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 saponification process at temperatures of from about 180° C. to about 350° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals while removing the water and separating the unsaponifiable part of the oxidation product from the saponified part.

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 saponification process at temperatures of from about 180° C. to about 350° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals, substantially in the absence of water, separating the unsaponifiable part of the oxidation product from the saponified part and setting free the acids from the latter.

3. A process for recovering fatty acids, which comprises subjecting oxidized material comprising the saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons to a saponification process at temperatures of from about 180° C. to about 350° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals, substantially in the absence of water 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 entire oxidation product to a saponification process at temperatures of from about 180° C. to about 350° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals, while removing the water, separating the unsaponifiable part of the oxidation product from the saponified part and setting free the acids from the latter.

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 entire oxidation product to a saponification process at temperatures of from about 180° C. to about 350° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals in an amount by about 3 to 8 per cent in excess of that corresponding to the saponification number of the entire oxidation product, substantially in the absence of water, separating the unsaponifiable part of the oxidation product from the saponified part 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 in a closed, pressure-tight vessel to a saponification process by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkaline metals and alkaline

earth metals, substantially in the absence of water, at temperatures of from about 150° C. to about 300° C., care being taken that any water vapor produced by the saponification reaction is removed from the reaction vessel, finishing the reaction in the absence of super-atmospheric pressure, separating the unsaponificable part of the oxidation product from the saponified part and setting free the acids from the latter.

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 saponification process at temperatures of from about 280° C. to about 300° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals while removing the water and separating the unsaponifiable part of the oxidation product from the saponified part.

8. A process of 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 saponification process at temperatures of from about 280° C. to about 300° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals, substantially in the absence of water, separating the unsaponifiable part of the oxidation product from the saponified part and setting free the acids from the latter.

9. A process for recovering fatty acids, which comprises subjecting oxidized material comprising the saponifiable part of an oxidation product, obtainable by the liquid-phase oxidation of from liquid to solid, non-aromatic hydrocarbons to a saponification process at temperatures of from about 280° C. to about 300° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals, substantially in the absence of water 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 saponification process at temperatures of from about 280° C. to about 300° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals, while removing the water, separating the unsaponifiable part of the oxidation product from the saponified part and setting free the acids from the latter.

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 saponification process at temperatures of from about 280° to about 300° C. by means of an alkaline reacting agent selected from the group consisting of the oxides, hydroxides and carbonates of the alkali metals and alkaline earth metals in an amount by about 3 to 8 percent in excess of that corresponding to the saponification number of the entire oxidation product, substantially in the absence of water, separating the unsaponifiable part of the oxidation product from the saponified part and setting free the acids from the latter.

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