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PROCESS FOR SEPARATING THE HYDROXY-ACIDS FROM THE OXIDATION PRODUCTS OF HYDROCARBONS

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This invention relates to a process for separating the hydroxy-acids from the oxidation products of hydrocarbons, especially paraffin, or waxes and similar substances.

By oxidizing paraffin and other hydrocarbons, waxes or similar substances with oxygen or oxygen-containing gases, mixtures are obtained which contain hydroxy-acids besides unsaponifiable portions, normal fatty acids and their esters. Of course, the percentage of such hydroxy-acids depends upon the oxidation method employed. As a rule, the percentage of oxidized acids increases the further the oxidation proceeds. For instance, applicants found in a paraffin, oxidized to a far-reaching degree, about 30% of hydroxy-acids.

Hitherto the main object of oxidizing hydrocarbons and similar substances was to obtain fatty acids from which soaps and the like could be produced. Hyrdoxy-acids, however, are not suitable for making grained soap and for distilling fatty acids.

Now we have ascertained, that from the raw mixture of various products obtained by treating with oxidizing gases paraffin or other hydrocarbons, waxes and similar substances, before or after the separation of the unsaponifiable matter, the hydroxy-acids may be separated, to a far-reaching extent and in a simple and economic manner, by heating the mixture with low-boiling hydrocarbons (boiling point lower than 125° C.), especially petroleum ether (boiling point lower than 60° C.), settling and decanting, or separating in any other way, the solution from the undissolved residue. Hereby, on the one hand, the hyrdoxy-acids are enriched to a considerable extent in the insoluble portion and, on the other hand, the portion, which is soluble in light benzine or petroleum ether, is freed from the main part of the oxidized acids, and therefore is considerably more useful for certain purposes, for instance, for making grained soap than the starting material. Moreover, the color of the refined product is greatly cleared.

We are aware that it has been proposed to separate the oxidation products of hydrocarbons into solid and liquid fatty acids by treating them with petroleum or similar hydrocarbons. From this process our invention differs in that we employ solvents, such as petroleum ether or low-boiling benzines, which dissolve fatty acids by far easier than hydroxy-acids. Therefore according to our process substantially the fatty acids (excluding the hydroxy-acids) are dissolved whereas the hydroxy-acids and the unsaponifiable constituents, which may still be present in the oxidized hydrocarbons, remain undissolved to a large extent.

It is a surprising fact that by a simple treatment with petroleum ether the hydroxy-acids can be precipitated in a high concentration from the mixture of oxidation products of hydrocarbons, waxes and similar substances. By oxidizing these materials various substances are formed which are all good solvents for hydroxy-acids. Therefore it was to be feared that these bodies would largely act as mediators of dissolution in the presence of petroleum ether.

Of course, the treatment with petroleum ether may be repeated several times or divided into several steps, whereby a complete separation of hydroxy-acids and fatty acids, not containing the OH-group, is attained.

The oxidation products may be subjected to the action of the petroleum ether under ordinary pressure or, for accelerating the dissolution, under a moderate pressure over atmospheric; in the latter case the hydroxy-acids are obtained in a highly concentrated state.

The hydroxy-acids obtained according to the present invention are distinguished from the commercial hydroxy-acids, hitherto on the market, by their higher percentage of pure hydroxy-acids and by a lighter color.

For instance, from the raw product resulting from oxidizing paraffin at 170° C., by means of a strong current of air in presence of catalysts, light-yellow or even nearly colorless hydroxy-acids were obtained.

Therefore by our new process not only the value of the oxidized hydrocarbons, waxes, and similar substances for certain purposes, for instance, in the manufacture of soap, is increased, but also hydroxy-acids are obtained which are superior to any hydroxy-acids heretofore obtained from other raw materials or by other separating methods.

The hydroxy-acids obtained according to the present invention may be used in the same way as the products rich in hydroxy-acids and obtained by natural or artificial oxidation of fatty oils, especially train-oil. They are extraordinarily adapted for making emulsions of various types, and may, for instance, like the commercial products known under the names "Degras" and "Moellon," be used alone or mixed with these compounds for fattening bark-tanned or chrome-tanned leather.

Examples

1. 100 grams of an oxidized paraffin obtained by treating paraffin with air at 180° C. were refluxed with petroleum ether (boiling between 30 and 50° C.). The resulting solution was decanted when hot from the molten undissolved residue, and the ether was removed from the residue and the extract by distillation. 42 grams of the residue and 58 grams of the extract were obtained. The properties of the raw material and the separated products were:—

	Color	Fusion point in degrees centigrade	Acid-number	Ester-number	Saponific.-number	Hydroxy-acids
Raw material	Dark-brown	39	84	141	225	20
Insoluble in petrol ether.	Dark-brown	18	109	165	274	35
Petrol ether extract.	Light-brown	39	63	106	169	12

The hydroxy-acids were tested after the Fahrion method (saponifying the products with ethyl-alcoholic caustic soda solution containing 80 grams NaOH per liter, evaporating the alcohol, dissolving the residue in little water, decomposing the soaps by hydrochloric acid, extracting the mixture with petroleum ether, removing the separated hydroxy acids, dissolving them in ethyl alcohol and evaporating the latter).

2. 300 grams of a product obtained by intensely treating paraffin with air in the presence of catalysts were shaken with 900 grams of hot petroleum ether for 15 minutes; then the solution was decanted when hot from the molten residue. By evaporating the ether 190 grams of an extract (I) were obtained. The undissolved residue, 110 grams, was anew treated in the same way with 300 grams of petroleum ether. Further 20 grams of an extract (II) and 90 grams of a residue insoluble in petroleum ether were obtained.

The properties of the raw material and the separated products were as follows:—

	Color	Fusion point in degrees centigrade	Acid-number	Ester-number	Saponific.-number	Hydroxy-acids
Raw material	Light yellow.	40	80	104	184	20
Insoluble in petrol ether.	Pale yellow	18	117	167	284	41
Petrol ether extract I.	Pale yellow	41	70	83	153	10
Petrol ether extract II.	Pale yellow	37	67	86	153	10

3. A wax fraction obtained by distilling Montan wax in a current of steam and showing a fusion-point of 58° C. was transformed, by treating it with air at 175° C. for 5 hours, into a yellow product showing

Fusion-point	51° C.
Acid-number	50
Saponification number	122
Contents of hydroxy-acids according to Fahrion	23%

(*a*) 100 grams of this oxidation product were refluxed according to the present invention for 30 minutes with 500 grams of a Pennsylvanian light benzine having a specific gravity of 0.686, highest boiling temperature 105° C. Two layers were formed which were separated from each other, the upper one containing almost the whole solvent, whereas the lower one had absorbed only a slight amount of the solvent. The solvent was evaporated from both layers. In this way products were obtained showing the following properties:—

	From the lower layer	From the upper layer
Color	Brown-yellow.	Yellow
Acid-number	71	48
Saponification number	176	118
Hydroxy-acid contents according to Fahrion about.	50%	15.8%

The output of matter soluble in light benzine was 91.4%, of that insoluble in light benzine 8.6%. The determination of the hydroxy-acids in the matter insoluble in benzine is believed to have furnished too high a value in this case, as the hydroxy-acids may have contained a certain amount of high-fusing fatty acids from the Montan wax distillate.

(*b*) By a moderate pressure at 35° C. 100 grams of the same oxidation product were separated, for removing the non-oxidized hydrocarbons, into 29 grams of a residue and 71 grams of a pasty waste. The latter only contained 20% of unsaponifiable matter,

whereas the residue from the pressing operation contained 62% of unsaponifiable matter. This treatment may be repeated, if desired.

Now the waste from the pressing operation was subjected to the treatment described sub (*a*) according to the present invention. We obtained, calculated upon the waste, 14.6% of matter insoluble in light benzine 85.4% of extract.

The matter insoluble in light benzine had a brownish-yellow color and a saponification number of 206, and contained 42% of hydroxy-acids, determined after the Fahrion method. The extract from the light benzine contained 13% of hydroxy-acids with a saponification number of 203.

4. An oxidation product obtained by treating ceresine with air at 175° C. for 8 hours, showing a dark-yellow color and containing 22% of hydroxy-acids and 33% of unsaponifiable matter was extracted with an 85% alcohol to remove the hydrocarbons contained therein. 85.5% of the oxidation product were dissolved. After distilling off the alcohol the extract still contained 22% of unsaponifiable matter, whereas in the residue, insoluble in alcohol, 60% unsaponifiable matter were determined substantially consisting of non-oxidized hydrocarbons.

The extract obtained by the alcohol treatment was separated into two portions by twice extracting it, each time with the threefold amount of light benzine of 0.686 specific gravity and uniting the extracts thus obtained. The portion soluble in light benzine showed a fusion-point of 39° C. and contained 12% of hydroxy-acids, whereas the matter insoluble in light benzine showed a fusion-point of 32° C. and contained 41% of hydroxy-acids.

When the ceresine oxidation product is treated with light benzine in the above-described manner, without, however, previously removing the high-fusing hydrocarbons, the portion insoluble in light benzine and enriched with hydroxy-acids shows a fusion-point of 83°, the extract obtained by the light benzine treatment showing a fusion-point of 53.5° C.

We claim:—

1. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in heating the said oxidized products with low-boiling benzines which are bad solvents for the hydroxy-acids, and separating the resulting solution from the undissolved matter.

2. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in heating the said oxidized products with petroleum ether, and separating the resulting solution from the undissolved matter.

3. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in removing the unsaponifiable matter from the said oxidized products, heating the residue with low-boiling benzines which are bad solvents for the hydroxy-acids, and separating the resulting solution from the undissolved matter.

4. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in removing the unsaponifiable matter from the said oxidized products, heating the residue with petroleum ether, and separating the resulting solution from the undissolved matter.

5. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in heating the said oxidized products under superatmospheric pressure with low-boiling benzines which are bad solvents for the hydroxy-acids, and separating the resulting solution from the undissolved matter.

6. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in heating the said oxidized products with petroleum ether under superatmospheric pressure, and separating the resulting solution from the undissolved matter.

7. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in removing the unsaponifiable matter from the said oxidized products, heating the residue under superatmospheric pressure with low-boiling benzines which are bad solvents for the hydroxy-acids, and separating the resulting solution from the undissolved matter.

8. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons, the steps which consist in removing the unsaponifiable matter from the said oxidized products, heating the residue with petroleum ether under superatmospheric pressure, and separating the resulting solution from the undissolved matter.

9. In the process for separating the fatty acids and hydroxy-acids contained in the products obtained by oxidizing hydrocarbons in the presence of a catalyst, the steps which consist in heating the said oxidized products with low-boiling benzines which are bad solvents for the hydroxy-acids, and separating the resulting solution from the undissolved matter.

In testimony whereof we affix our signatures.

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