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WORKING UP OF OXIDATION PRODUCTS OF HYDROCARBONS

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9 Claims. (Cl. 260—116)

The present invention relates to the working up of oxidation products of hydrocarbons.

In the recovery of acids from the products of a destructive oxidation by means of oxygen, or gaseous mixtures containing the same of difficultly volatile i. e. liquid or solid hydrocarbons, or hydrocarbon mixtures, as for example paraffin wax, by distillation there is the drawback that resinification, the formation of pitch and the like readily occur and lead to a loss in the fatty acids.

I have now found that the said drawback is avoided by subjecting the oxidation products or an acid fraction separated therefrom, before working up by distillation or other process for working the products such as saponification or hydrogenation, to a pretreatment by heating while avoiding losses by distillation as for example by allowing them to stand for several hours at from 150° to 250° C., at any pressure and preferably in the presence of catalysts promoting the splitting off of water from hydroxyl-bearing organic compounds, such as mineral acids or their anhydrides, sulphonic acids or zinc chloride. The said pretreatment may be carried out in the absence of oxygen or may also be combined with other processes, as for example a bleaching with gaseous strong reducing agents such as hydrogen or sulphur dioxide, or agents furnishing the same, such as bisulphites, at temperatures above 100° C. It is very important to avoid local overheating during the pretreatment, so that it is preferable to keep the product to be treated in motion during the heating, as for example by stirring, shaking or the like. The advantages obtained by the treatment according to the present invention consist not only in the fact that the products obtained may be distilled without residue but also in the fact that the soaps may be salted out more readily. The amount of pitch formed during the distillation only amounts to a few per cent.

Oxidation products of aliphatic or naphthenic hydrocarbons, as for example of petroleum fractions, such as middle oil, paraffin wax, ceresine and the like, or of naphthene hydrocarbons such as paraffin oil, or Russian gas oil, or of synthetic oils, as for example hydrocarbon mixtures obtained by the hydrogenation of tars, or of brown coal tar fractions, may be employed as the initial materials. Generally speaking, temperatures of between 150° and 300° C., especially those between 200° and 250° C., are employed for the heating.

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 oxidizing gas oil contained in a vessel completely filled with Raschig rings or similar fillers by means of air blown through the oil at 150° C. are treated for 4 hours at 250° C. under a pressure of 50 atmospheres with finely divided metallic nickel and hydrogen in the presence of 5 parts of naphthalene mono-sulphonic acid. 480 parts of a greatly clarified product are obtained showing the following differences from the initial material:

	Solubility in petroleum ether	Iodine value	Pitch obtained when distilled
	Percent		*Percent*
Initial material	58.2	17.8	20
Treated product	91.8	46.7	3

By distillation in vacuuo, 95 parts of a distillate which is practically soluble in petroleum ether are obtained from each 100 parts of treated product.

Example 2

An oxidation product obtianed by oxidizing paraffin wax at about 160° C. in the manner described in the foregoing example are heated to boiling at 250° C. under a vacuum of from 150 to 200 millimetres mercury gauge for 4 hours, while stirring and employing a reflux condenser. The solubility of the oxidation product rises from 92.3 to 98.3 per cent. When the crude acids separated from the oxidation product are distilled, a residue of only 1.7 per cent of pitch remains in contrast to 18 per cent remaining if the pretreatment be not carried out.

Example 3

An oxidation product from paraffin wax obtained as described in Example 2 is heated at 250° C. for 4 hours, while stirring, under a pressure of 50 atmospheres of carbon dioxide. The solubility in petroleum ether rises from 92.2 to 98.2 per cent. The residue which remains when

the crude acids are distilled amounts only to 2.5 per cent of pitch.

Example 4

500 parts of the crude mixture of carboxylic acids, obtained from an oxidation product of paraffin prepared by treating the latter with air at 140° C., saponifying the resulting oxidation product with aqueous alcoholic caustic soda solution, removing unsaponifiable constituents by extraction with benzine and acidifying the soap solution with sulphuric acid, are heated for 2 hours while stirring to 250° C. while replacing air in the vessel by nitrogen. The solubility of the product in petroleum ether is increased from 91.7 to 98.6 per cent and the product offers no difficulties in further working up.

What I claim is:—

1. In working up products from the liquid phase oxidation of difficultly volatile hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the said oxidation products to a temperature above 150° C. while avoiding a distillation.

2. In working up products from the liquid phase oxidation of difficultly volatile hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the said oxidation products in the presence of a catalyst, capable of promoting the splitting off of water from hydroxyl bearing organic compounds, to a temperature above 150° C. while avoiding a distillation.

3. In working up products from the liquid phase oxidation of difficultly volatile hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the acid fraction of the said oxidation products to a temperature above 150° C. while avoiding a distillation.

4. In working up products from the liquid phase oxidation of difficultly volatile hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the said oxidation products to a temperature between 200° and 250° C. while avoiding a distillation.

5. In working up products from the liquid phase oxidation of difficultly volatile hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the said oxidation products in the presence of a catalyst, capable of promoting the splitting off of water from hydroxyl bearing organic compounds, to a temperature between 200° and 250° C. while avoiding a distillation.

6. In working up products from the liquid phase oxidation of difficultly volatile hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the said oxidation products in the presence of a gaseous strong reducing agent to a temperature above 100° C. while avoiding a distillation.

7. In working up products from the liquid phase oxidation of difficultly volatile hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the said oxidation products in the presence of hydrogen to a temperature above 100° C. while avoiding a distillation.

8. In working up products from the liquid phase oxidation of difficultly volatile aliphatic hydrocarbons by means of anhydrous gaseous oxidizing agents containing free oxygen, the step which comprises heating the said oxidation products to a temperature between 200° and 250° C. while avoiding a distillation.

9. In working up products from the liquid phase oxidation of paraffin wax by means of anhydrous gaseous oxidizing agents containing free oxygen and separating the acids formed, the step which comprises heating the acid fraction of the said oxidation product to a temperature between 200° and 250° C. while avoiding a distillation.

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