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OXIDATION OF LIQUID HYDROCARBONS

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The present invention relates to the oxidation of liquid hydrocarbons.

In the copending application Ser. No. 311,966, filed Oct. 11, 1928, we have suggested a process for the oxidation of liquid hydrocarbons of the benzine series boiling below 180° C., either as such or in the form of mixtures thereof, according to which the said materials are exposed in the liquid phase at elevated temperatures, such as between 80° and 200° C., preferably at about 145° C., to the action of a gaseous oxidizing agent such as oxygen, air, nitrogen oxides or mixtures thereof, if desired at superatmospheric pressure, such as up to about 50 atmospheres, and/or in the presence of a metallic or organic catalyst such as organic compounds of the alkali or alkaline earth metals or of magnesium, aluminium or manganese as for example their resinates, oleates or enolates, and solid bodies of aluminium having a large superficial area if desired together with similar but inert bodies such as those from glass, porcelain and the like. In any case the ratio of the oxidating agent to the said hydrocarbons and gaseous compounds present at the pressure and temperature employed is kept below the explosion point, the gaseous oxidating agents being diluted with inert gases especially on working at superatmospheric pressure, whereby any risk of explosion may be prevented.

We have now found that by carrying out the oxidation of the said hydrocarbons, or mixtures thereof such as petroleum fractions having a boiling range from 40° to about 130° C., from the start in the presence of a diluent consisting of at least 2 per cent their weight of an aliphatic saturated carboxylic acid, containing up to 4 carbon atoms in its molecule, the course of the reaction is influenced in such a manner that alcohols are mainly obtained as the oxidation products. As the diluents may be mentioned formic acid, acetic acid, propionic acid and the like, or their anhydrides, which are included by the term acids, since the anhydrides are converted into acids, or mixtures of the said substances. Generally, a quantity of from 10 to 20 per cent of the acids will give the best results, which quantity may be somewhat reduced when anhydrides, or mixtures containing the same, are employed. By carrying out the process in this manner there is the special advantage that the reaction proceeds mainly with the formation of esters because the acids and the like employed enter into reaction with the alcohols formed. No attack on the esters by the oxidizing gases takes place, and in particular practically no resinification, polymerization and the like takes place. The reaction product usually consists of two layers, one of which contains, concentrated therein, the oxidation products which may be readily separated from the residual initial material, which is free from resins, waxes or other polymerization products which, on working in a manner different from the process according to the present invention, are usually formed in rather considerable quantities. The oxidation products constitute, after their separation, liquids of very low viscosity, such as butyl acetate and acetates of similar homologous alcohols when acetic acid has been employed as the diluent, and other oxygenated products of low molecular weight.

The precise conditions of working as regards temperature, pressure, addition of catalysts and gaseous oxidizing agents may be the same as described in our copending application Ser. No. 311,966 filed October 11, 1928, but the process according to the present invention is applicable to any oxidation of the said initial material.

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

300 parts of hexane to which have been added 30 parts of acetic acid and 0.15 part of manganese acetyl acetonate are treated with a current of air, the quantity of which amounts to 100 parts per hour, during the course of 5 hours at about 145° C. under a pressure of 20 atmospheres in a pressure-tight tube lined with aluminium and charged with filling bodies of the nature of Raschig rings. The gas leaving the cooled

upper part of the furnace contains from 0.5 to 2 per cent of oxygen. Besides unchanged hexane, the product consists mainly of esters of acetic acid with lower alcohols. The esters may be readily separated from hexane by distillation. The reaction can be carried out without a catalyst, though it is advantageous to employ such catalyst, whereby the oxygen content of the gaseous oxidizing agent is more fully consumed in the oxidation, so that explosions of the waste gases are avoided.

Example 2

320 parts of a petroleum fraction having a boiling point from 70° to 75° C. are treated in the apparatus described in Example 1 together with 0.25 part of manganese acetyl acetonate and 25 parts of acetic anhydride for 4½ hours at 150° C. and at a pressure of 50 atmospheres with 130 parts per hour of a mixture of 62 parts by volume of air and 38 parts of carbon dioxide. After cooling, the reaction product forms two layers the upper of which mainly consists of unaltered initial material whereas the lower layer mainly consists of carboxylic acids and their esters.

Example 3

300 parts of the petroleum fraction referred to in Example 2 are blown with air for 3 hours at a temperature of from 145° to 150° C. and at a pressure of from 25 to 30 atmospheres after they have been incorporated with a mixture of 25 parts of propionic acid and 10 parts of acetic anhydride and with 0.6 part of barium cinnamate. The reaction product possesses a composition similar to that obtainable in accordance with the foregoing example.

What we claim is:—

1. In the oxidation of liquid hydrocarbons of the benzine series boiling below 180° C. in the liquid state with the aid of a gaseous oxidizing agent while heating, the step which comprises incorporating the initial material before the oxidation with at least 2 per cent its weight of an aliphatic, saturated carboxylic acid containing up to 4 carbon atoms in its molecule.

2. In the oxidation of liquid hydrocarbons of the benzine series boiling below 180° C. in the liquid state with the aid of a gaseous oxidizing agent and an oxidation catalyst while heating, the step which comprises incorporating the initial material before the oxidation with at least 2 per cent its weight of an aliphatic, saturated carboxylic acid containing up to 4 carbon atoms in its molecule.

3. In the oxidation of liquid hydrocarbons of the benzine series boiling below 180° C. in the liquid state with the aid of a gaseous oxidizing agent while heating, the step which comprises incorporating the initial material before the oxidation with at least 2 per cent its weight of an anhydride of an aliphatic, saturated carboxylic acid containing up to 4 carbon atoms in its molecule.

4. In the oxidation of a petroleum fraction having a boiling range from 40° to 130° C. with the aid of a gaseous oxidizing agent while heating, the step which comprises incorporating the initial material before the oxidation with at least 2 per cent its weight of an aliphatic, saturated carboxylic acid containing up to 4 carbon atoms in its molecule.

5. In the oxidation of a petroleum fraction having a boiling range from 40° to 130° C. with the aid of a gaseous oxidizing agent while heating, the step which comprises incorporating the initial material before the oxidation with at least 2 per cent its weight of acetic acid.

6. In the oxidation of liquid hydrocarbons of the benzine series, boiling below 180° C., in the liquid state with the aid of a gaseous oxidizing agent while heating, the step which comprises incorporating the initial material before the oxidation with from 2 to 10 per cent its weight of an aliphatic, saturated carboxylic acid containing up to 4 carbon atoms in its molecule.

7. In the oxidation of a petroleum fraction, having a boiling range from 40° to 130° C., with the aid of air, while heating, the step which comprises incorporating the initial material before the oxidation with from 2 to 10 per cent its weight of acetic acid.

8. In the oxidation of a petroleum fraction, having a boiling range from 40° to 130° C., with the aid of air at about 150° C. and at a pressure between about 25 and 30 atmospheres, the step which comprises incorporating the initial material before the oxidation with from 2 to 10 per cent its weight of acetic acid.

9. In the oxidation of a petroleum fraction, having a boiling range from 40° to 130° C., with the aid of air at about 150° C., and at a pressure between about 25 and 50 atmospheres the step which comprises incorporating the initial material before the oxidation with manganese acetyl acetonate and from 7 to 10 per cent of the weight of said petroleum fraction of acetic acid.

In testimony whereof we have hereunto set our hands.

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