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OXIDATION OF PETROLEUM HYDROCARBONS

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6 Claims. (Cl. 196—142)

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The present invention relates to improvements in the oxidation of petroleum hydrocarbons, and more particularly relates to improvements in the process of oxidizing hydrocarbons by blowing the hydrocarbons with air while at an elevated temperature. The invention is applicable to the production of fatty acids, for use, for instance, as soap stock and also from which edible and inedible fats may be prepared, from non-saponifiable petroleum hydrocarbons, both saturated and unsaturated.

The oxidation of petroleum hydrocarbon by blowing with air in the presence of a catalyst and under conditions of high temperature and high pressure has previously been proposed and has met with some degree of success. However, the necessity of operating at high temperatures and under high pressures, and the prolonged period over which the process must be continued, have been decided disadvantages. Because of the high temperature and high pressure requirements, expensive apparatus must be employed, and because of the prolonged blowing period using air alone under such conditions, the apparatus and process costs are excessive.

I have discovered that petroleum hydrocarbons can be oxidized more readily and without the use of troublesome high temperature and high pressures by including in the air with which the hydrocarbon is blown a minor proportion of chlorine dioxide. By the inclusion of the chlorine dioxide, substantial oxidation of non-saponifiable petroleum hydrocarbons to fatty acids may be effected at atmospheric pressure and at temperatures as low as 100° C. and somewhat lower. Further, the oxidation is effected much more rapidly.

Predicated on this discovery, my present invention comprises, in its broader aspect, an improvement in the process for oxidizing hydrocarbons by blowing with air which comprises the step of adding a minor proportion of chlorine dioxide to the air with which the hydrocarbon is customarily blown. In its more advantageous aspect, my invention comprises an improved process of the type just described, wherein the hydrocarbon, under atmospheric pressure and at a temperature not exceeding about 100° C., is blown with air to which there has been added a minor proportion of chlorine dioxide.

My invention is applicable to high molecular weight petroleum hydrocarbons, for instance, those containing 8 or more carbon atoms per molecule and including paraffin waxes, petrolatum and the like. The invention is also useful in the oxidation of asphalt by including a minor

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proportion of chlorine dioxide in the air with which the asphalt is blown in conventional practice. Where the hydrocarbons being oxidized are normally solid, or semi-solid, at normal temperatures, the operating temperatures should be sufficiently high to reduce the hydrocarbon to the liquid condition.

The concentration of chlorine dioxide in the chlorine dioxide-air mixture may be varied somewhat but, in order to avoid hazardous handling conditions, should not exceed that at which the partial pressure of the chlorine dioxide is about 30 mm. of mercury, if temperatures in excess of 100° C. are to be used. At temperatures around 50° C. or lower, higher concentrations of chlorine dioxide in the chlorine dioxide-air mixture may be used, for instance, proportions sufficient to give a chlorine dioxide partial pressure of 50 mm. of mercury may be safely employed. The minimum effective concentration of chlorine dioxide depends somewhat upon the particular hydrocarbon being oxidized and also upon the temperature employed but advantageously should be at least sufficient to give a chlorine dioxide partial pressure of about 5 mm. of mercury in the chlorine dioxide-air mixture used.

The oxidation of the hydrocarbons is, with advantage, carried out in the presence of a known oxidation catalyst, for instance, one of those conventionally used in the oxidation of hydrocarbon by blowing with air alone, such as iron oxide, ferric naphthenate, or manganese oleate, stearate or naphthenate. However, my process has been found to be highly effective even in the absence of such oxidation catalyst.

The operating temperatures and the rate of oxidation are somewhat interdependent, the optimum operating conditions being dependent upon the particular hydrocarbon being oxidized. In general, the rate of oxidation appears to increase with the operating temperature and the rate of blowing the hydrocarbon with the chlorine dioxide-air mixture. The optimum rate of blowing is also dependent somewhat upon the particular hydrocarbon or hydrocarbon mixture being oxidized. If too high a blowing rate is employed, some chlorine dioxide will be present in the effluent gases which is generally to be avoided.

The invention is applicable to highly refined hydrocarbons, but is usually used to greater advantage in the oxidation of only partially refined, or more or less crude hydrocarbons for the reason that such less highly refined hydrocarbons

are usually more readily oxidized and also are available at lower cost.

My invention will be further described and illustrated by the following specific examples of this application to the oxidation of various petroleum hydrocarbons. In each instances, the oxidation was carried out at a temperature of about 75 to 80° C. and at substantially atmospheric pressure. The proportion of chlorine dioxide in the chlorine dioxide-air mixture used was, in each instance, such that the partial pressure of the chlorine dioxide was about 30 mm. of mercury.

Example I

100 grams of a highly refined kerosene of zero iodine value and zero acid value was placed in a flask and blown with the chlorine dioxide-air mixture for a period of 52 hours, no oxidation catalyst being employed. Over this period, the calculated amount of chlorine dioxide used was about 77 grams. At the end of the oxidation period, the hydrocarbon was found to be oxidized sufficiently to give an acid value of 21.25.

Example II

100 grams of a highly refined microcrystalline wax was placed in a flask, melted and blown with the chlorine dioxide-air mixture for a period of 52 hours, no oxidation catalyst being employed. Over this period, about 115 grams of chlorine dioxide was used. The wax, which originally had an acid value of 0.49, was thereafter found by analysis to have an acid value of 5.30.

Example III

100 grams of a petroleum light lubricating oil fraction having a fatty acid value of 0.24, was blown with the chlorine dioxide-air mixture for a period of 36 hours, during which time about 46 grams of chlorine dioxide was used, no oxidation catalyst being employed. At the end of the blowing period, the hydrocarbon was found by analysis to have an acid value of 67.19.

For purposes of comparison, a 100 gram sample of the light lubricating oil fraction used in Example III was blown for 36 hours under similar conditions with air alone, at the end of which period the acid value of the hydrocarbon was found by analysis to be only 1.23.

As previously noted, the rate of oxidation of the hydrocarbons by blowing with the chlorine dioxide-air mixture in accordance with my invention is increased by the presence in the hydrocarbons of small amounts of known oxidation catalyst. This has been shown, for instance, by blowing separate samples of the hydrocarbon fraction used in Example III with mixtures of chlorine dioxide and air, such as there used, for comparable periods of time, one of the samples containing no oxidation catalyst and the other containing 1%, by weight, of manganese oleate. In the catalyzed operation, the acid value was increased to 19.90, while the product of the uncatalyzed operation had an acid value of 7.23.

The acid values noted above were determined by the prescribed method, the values given indicating the number of milligrams of KOH required to neutralize one gram of the sample.

I claim:

1. A process for the oxidation of petroleum hydrocarbons which comprises blowing a hydrocarbon containing not less than eight carbon atoms per molecule, while at substantially atmospheric pressure at an elevated temperature not exceeding 100° C. with a mixture of chlorine dioxide and air in which the partial pressure of the chlorine dioxide is within the range of 5 to 30 mm.

2. A process for the oxidation of petroleum hydrocarbons which comprises blowing the hydrocarbons with air containing a minor proportion of chlorine dioxide effective to promote the oxidation while controlling the partial pressure of chlorine dioxide in the chlorine dioxide-air mixture within the range of 5 to 50 mm. of mercury at elevated temperatures around 50° C. and lower and 5 to 30 mm. of mercury at the hgher temperatures not substantially exceeding 100° C.

3. A process for the oxidation of petroleum hydrocarbons which comprises blowing the hydrocarbons at an elevated temperature not exceeding 100° C. with a mixture of chlorine dioxide and air in which the partial pressure of the chlorine dioxide is within the range of 5 to 30 mm. of mercury.

4. A process for the oxidation of petroleum hydrocarbons which comprises blowing the hydrocarbons with air in the presence of an oxidation catalyst, the air containing a minor proportion of chlorine dioxide effective to promote the oxidation, while controlling the partial pressure of chlorine dioxide in the chlorine dioxide-air mixture within the range of 5 to 50 mm. of mercury at elevated temperatures around 50° C. and lower and 5 to 30 mm. of mercury at the higher temperatures not substantially exceeding 100° C.

5. A process for the oxidation of petroleum hydrocarbons which comprises blowing the hydrocarbons with air in the presence of an oxidation catalyst, the air containing a minor proportion of chlorine dioxide effective to promote the oxidation, while controlling the partial pressure of chlorine dioxide in the chlorine dioxide-air mixture within the range of 5 to 30 mm. of mercury and maintaining an elevated temperature not exceeding 100° C.

6. A process for the oxidation of petroleum hydrocarbons which comprises blowing the hydrocarbons at an elevated temperature of about 75 to 80° C. with a mixture of chlorine dioxide and air in which the partial pressure of the chlorine dioxide is about 30 mm. of mercury

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,573,751 November 6, 1951

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 4, line 10, for "30 mm." read *30 mm. of mercury.*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of February, A. D. 1952.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.