RESERVE COPY

PATENT SPECIFICATION

Application Date: July 14, 1936. No. 19560/36.

478,317

Complete Specification Left: June 8, 1937.

Complete Specification Accepted: Jan. 14, 1938.

1129

PROVISIONAL SPECIFICATION

Improvements in the Manufacture and Production of Oxidation Products from Paraffin Hydrocarbons of High Molecular Weight

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

My foreign correspondents have now found that oxidation products which are valuable industrially can be obtained by carrying out the oxidation while using alkali compounds of manganese which contain the manganese in the anion and the alkali as the cation. Suitable catalysts are for example potassium, sodium or ammonium permanganate, potassium or sodium manganate or manganite or potassium manganese cyanide. The said manganese alkali compounds may be used alone, in admixture with each other or together with other oxidation catalysts, such as manganese acetate, or together with substances having an alkaline reaction, such as soda. Generally speaking additions of from about 0.025 to 0.50 per cent. with reference to the hydrocarbon to be oxidised are sufficient.

The oxidation is carried out at temperatures between 80° and 115° Centigrade. As oxidising gases there may be mentioned oxygen, air or other gases containing oxygen, which may also contain small amounts of substances having an accelerating action, as for example oxides of nitrogen. The oxidation may be carried out at atmospheric, reduced or increased pressure and proceeds comparatively rapidly in spite of the low temperatures used. The supply of the oxidising gas is preferably effected through devices or bodies which effect a fine dispersion of the gas, as for example sinter plates, filter candles, nozzles or filler bodies. When the oxidation is completed, the resulting products are saponified in the usual manner and the unsaponifiable constituents separated from the soaps. The manganese catalyst is exclusively contained in the unsaponifiable constituent; it may be recovered therefrom by filtration and may be used again for the oxidation.

It is preferable to heat the paraffin hydrocarbons after the addition of the catalyst, but before the action of the oxidising gas, to high temperatures, as for example to from 100° to 200° Centigrade, for a long time advantageously while stirring. In the case of many hydrocarbons a longer pretreatment of this kind, as for example lasting several hours, is advantageous. The pretreatment may usually be considerably shortened by adding to the paraffin hydrocarbons the unsaponifiable constituents from a previous batch in amounts of from about 10 to 50 per cent. In many cases it is sufficient to pretreat only a part of the hydrocarbons to be oxidised (if desired after the addition of a small amount of the unsaponifiable constituents obtained from an earlier batch) with the said alkali manganese compounds, the pretreated part together with the untreated initial material then being subjected to oxidation.

The oxidation products obtained in the said manner have a pale colour and yield directly by saponification pale and odourless soaps. From the latter, pale fatty acids may be obtained which distil well.

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.

100 parts of a yellow-brown crude paraffin wax having a melting point of 50° Centigrade are heated for 2 hours at 150° Centigrade while stirring well together with 0.15 part of finely powdered potassium permanganate and 0.05 part of caustic potash. The mass is then cooled to about 100° Centigrade and introduced into the oxidation vessel shewn diagrammatically in the accompanying drawing in which air is blown for 8 hours at a temperature of from 110°

[*Price* 1/-]

to 115° Centigrade. The mass is introduced at B into the cylindrical vessel A which is surrounded by a heating jacket H for the purpose of maintaining the necessary temperature and the product leaves the cylindrical vessel at the bottom. The air is introduced through the porous plate C and the residual gas leaves at D and may then be led through a separating device (not shewn). A part of the hydrocarbon to be oxidised is continuously circulated through the overflow pipe E. The pipe F opening into the overflow pipe E returns to the oxidation chamber any product which has passed over into the trap G. The oxidation product obtained is only slightly yellow in colour; it has an acid value of 95 and a saponification value of 152.

From this product there may be obtained in known manner a pale fatty acid having a saponification value of 220 and containing only 0.1 per cent. of constituents insoluble in petroleum ether. By distilling this fatty acid *in vacuo* a pure white fatty acid is obtained which is well suited for example for the preparation of soaps.

EXAMPLE 2.

50 parts of a hard paraffin wax obtained from low temperature carbonisation tar and 50 parts of an unsaponifiable oxidation product obtained from a previous batch are heated for about 10 minutes to 150° Centigrade while stirring well after the addition of 0.12 part of sodium manganate. The dark coloured product is then filtered and oxidised at a temperature of from 95° to 100° Centigrade with a gas mixture consisting of 50 per cent. of oxygen and 50 per cent. of nitrogen which is introduced through a porous filter plate at the bottom of the oxidation vessel. After about 22 hours, the oxidation is discontinued and a practically colourless product having an acid value of 74 is obtained. The soap obtained therefrom in the usual way has a pale colour and a pleasant odour and a good washing power.

EXAMPLE 3.

50 parts of a paraffin wax obtained from the hydrogenation product of brown coal are heated for 2 hours at 160° Centigrade after the addition of 0.5 per cent. of potassium permanganate. After filtration, the treated paraffin wax is mixed with 50 parts of the same paraffin wax which has not been so pretreated and oxidised by blowing in air of a fine dispersion between 100° and 112° Centigrade. After about 7½ hours, a product is obtained having an acid value of 81 which yields by the usual working up pale soaps having good washing action.

Dated this 14th day of July, 1936.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Agents

COMPLETE SPECIFICATION

Improvements in the Manufacture and Production of Oxidation Products from Paraffin Hydrocarbons of High Molecular Weight

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company, organized under the Laws of Germany) and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

In specification No. 369,852 it has been proposed to produce fatty acids and the like from paraffin wax, by hydrogenating hydrocarbon oil containing waxy constituents and oxidising the hydrogenated wax in the presence of potassium permanganate. The oxidation may be carried out at temperatures as low as about 250° F. but preferably at about 350° F. or higher.

My foreign correspondents have now found that oxidation products from paraffin hydrocarbons of high molecular weight which are valuable industrially can be obtained by carrying out the oxidation at a temperature not above 115° Centigrade while using as catalysts alkali compounds of manganese which contain the manganese in the anion and the alkali as the cation. Suitable catalysts are for example potassium, sodium or ammonium permanganate, potassium or sodium manganate or manganite or potassium manganese cyanide. The said manganese alkali compounds may be used alone, in admixture with each other or together with other oxidation catalysts, such as manganese acetate, or together with substances having an alkaline reaction, such as soda. Generally speaking addition of from about 0.025 to 0.50 per cent. with reference to the hydrocarbons to be oxidised are sufficient.

The oxidation is carried out at temperatures between 80° and 115° Centigrade. As oxidising gases there may be mentioned oxygen, air or other gases containing oxygen, which may also contain small amounts of substances having an accelerating action, as for example oxides of nitrogen. The oxidation may be carried out at atmospheric, reduced or increased pressure and proceeds comparatively rapidly in spite of the low temperatures used. The supply of the oxidising gas is preferably effected through devices or bodies which effect a fine dispersion of the gas, as for example sinter plates, filter candles, nozzles or filler bodies. When the oxidation is completed, the resulting products are saponified in the usual manner and the unsaponifiable constituents separated from the soaps. The manganese catalyst is exclusively contained in the unsaponifiable constituent; it may be recovered therefrom by filtration and may be used again for the oxidation.

It is preferable to heat the paraffin hydrocarbons after the addition of the catalyst, but before the action of the oxidising gas, to high temperatures, as for example to from 100° to 200° Centigrade, for a long time advantageously while stirring. In the case of many hydrocarbons a longer pretreatment of this kind, as for example lasting several hours, is advantageous. The pretreatment may usually be considerably shortened by adding to the paraffin hydrocarbons the unsaponifiable constituents from a previous batch in amounts of from about 10 to 50 per cent. In many cases it is sufficient to pretreat only a part of the hydrocarbons to be oxidised (if desired after the addition of a small amount of the unsaponifiable constituents obtained from an earlier batch) with the said alkali manganese compounds, the pretreated part together with the untreated initial material then being subjected to oxidation.

The oxidation products obtained in the said manner have a pale colour and yield directly by saponification pale and odourless soaps. From the latter, pale fatty acids may be obtained which distil well.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

100 parts of a yellow-brown crude paraffin wax having a melting point of 50° Centigrade are heated for 2 hours at 150° Centigrade while stirring well together with 0.18 part of finely powdered potassium permanganate and 0.05 part of caustic potash. The mass is then cooled to about 100° Centigrade and introduced into the oxidation vessel shewn diagrammatically in the drawing accompanying the provisional specification No. 19560 A.D. 1936 in which air is blown for 8 hours at a temperature of from 110° to 115° Centigrade. The mass is introduced at B into the cylindrical vessel A which is surrounded by a heating jacket H for the purpose of maintaining the necessary temperature and the product leaves the cylindrical vessel at the bottom. The air is introduced through the porous plate C and the residual gas leaves at D and may then be led through a separating device (not shown). A part of the hydrocarbon to be oxidised is continuously circulated through the overflow pipe E. The pipe F opening into the overflow pipe E returns to the oxidation chamber any product which has passed over into the trap G. The oxidation product obtained is only slightly yellow in colour; it has an acid value of 95 and a saponification value of 152.

From this product there may be obtained in known manner a pale fatty acid having a saponification value of 220 and containing only 0.1 per cent. of constituents insoluble in petroleum ether. By distilling this fatty acid *in vacuo* a pure white fatty acid is obtained which is well suited for example for the preparation of soaps.

EXAMPLE 2.

50 parts of a hard paraffin wax obtained from low temperature carbonisation tar and 50 parts of an unsaponifiable oxidation product obtained from a previous batch are heated for about 10 minutes to 150° Centigrade while stirring well after the addition of 0.12 part of sodium manganate. The dark coloured product is then filtered and oxidised at a temperature of from 98° to 100° Centigrade with a gas mixture consisting of 50 per cent. of oxygen and 50 per cent. of nitrogen which is introduced through a porous filter plate at the bottom of the oxidation vessel. After about 22 hours, the oxidation is discontinued and a practically colourless product having an acid value of 74 is obtained. The soap obtained therefrom in the usual way has a pale colour and a pleasant odour and a good washing power.

EXAMPLE 3.

50 parts of a paraffin wax obtained from the hydrogenation product of brown coal are heated for 2 hours at 160° Centigrade after the addition of 0.5 per cent. of potassium permanganate. After filtration, the treated paraffin wax is mixed with 50 parts of the same paraffin wax which has not been so pretreated and oxidised by blowing in air of a fine dispersion between 100° and 112° Centigrade. After about 7½ hours, a product is obtained having an acid value of 81 which yields by the usual working up pale soaps having good washing action.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The process for the manufacture and production of oxidation products from paraffin hydrocarbons of high molecular weight which comprises carrying out the oxidation at a temperature not above 115° Centigrade while using as catalysts alkali compounds of manganese which contain the manganese in the anion and the alkali as the action.

2. In the process as claimed in claim 1, heating the paraffin hydrocarbons, or a part thereof, in the presence of the catalysts but before the action of the oxidising gas, to high temperatures.

3. In the process according to claim 2, adding to the paraffin hydrocarbons the unsaponifiable constituents from the previous batch.

4. In the process as claimed in any of the preceding claims, employing sodium permanganate.

5. In the process as claimed in any of the preceding claims, employing the manganese compounds together with other oxidation catalysts.

6. The process for the manufacture and production of oxidation products from paraffin hydrocarbons of high molecular weight substantially as described in each of the foregoing Examples.

7. Oxidation products of paraffin hydrocarbons of high molecular weight when obtained according to the process particularly described and ascertained.

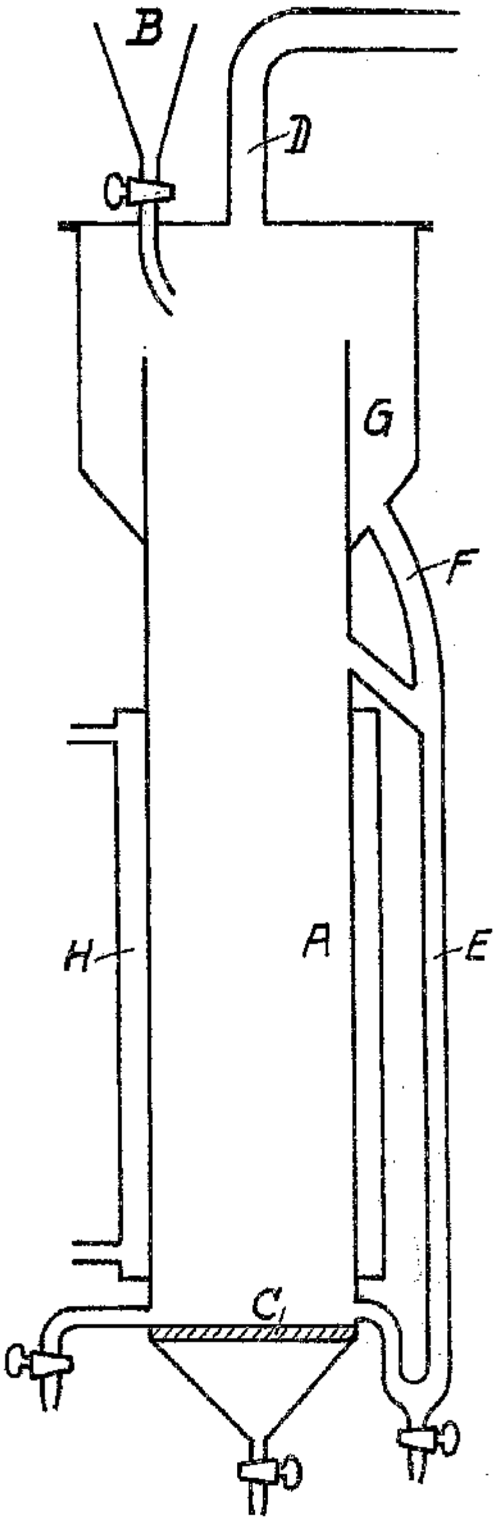
Dated the 8th day of June, 1937.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London,
W.C.2,
Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1938.

478,317 PROVISIONAL SPECIFICATION

1 SHEET

[This Drawing is a full-size reproduction of the Original.]



Malby & Sons, Photo-Lith.