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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Oxidation Products of Hydrocarbons of High Molecular Weight

(A communication to me from abroad by WILHELM AD. FARENHOLTZ, GUSTAV HUBBE, and HERBERT HUBBE, all German Citizens trading as the Firm VEREINIGTE OELFABRIKEN HUBBE & FARENHOLTZ, of 66, Reichspräsidentenstrasse, Magdeburg - Friedrichstadt, Germany).

I, WILLIAM HANS ARNOLD THIEMANN, Chartered Patent Agent, of the Firm Albert L. Mond & Thiemann, of 19, Southampton Buildings, Chancery Lane, London, W.C.2, a British Subject, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process of and apparatus for the production of oxidation products, such as fatty acids or alcohols from hydrocarbons of high molecular weight by oxidation.

In the production of fatty acids or alcohols from hydrocarbons with the aid of gases containing oxygen—such as air, it is known to effect the oxidation at elevated temperatures between the melting point and boiling point of the material, and, in order to accelerate the reaction, to spray the hydrocarbons into the oxygen-bearing gas. For the oxidation of solid paraffin, it is also known to pass the hydrocarbons, in liquid condition, in counterflow to the oxidising gas, that is to say, to bring the air into contact, in the first place, with the most extensively oxidised material. It has also been established that, in oxidising hydrocarbons with compressed air, the yield of alcohols can be improved by adding from 2 to 10% of anhydrous, organic acids of low molecular weight to the air.

The known processes have the defect that considerable quantities of, mostly undesirable, dark-coloured and malodorous by-products for example, oxy-acids, are formed. Moreover, a comparatively long time is required for carrying out the oxidation. A large portion—about 40 to 50%—of the originating hydrocarbons is left unchanged in the oxidation products, the oxidation being therefore very incomplete.

The present invention enables the oxidation of hydrocarbons of high molecular weight to fatty acids, alcohols or the like, to be substantially improved.

It is known that the oxidation of hydrocarbons by means of gases containing oxygen, or of solid or liquid oxidising agents in association with inert gases, which flow through the reaction mixture, is favourably influenced, to an extraordinary degree, by certain readily volatile products which are primarily formed during the oxidation. Which of these products come individually into action has not yet been definitely ascertained, apparently the case is one of a mixture of alcohols, aldehydes, combinations of peroxides with the reaction water or steam and with volatile fatty acids and other oxidation products formed at the reaction temperature.

If, for example, a current of air be passed through a vessel in which the oxidation of hydrocarbons of high molecular weight takes place in known manner, and this current of air, laden with oxidation products which are volatile at the reaction temperature, be passed into a second vessel in which the oxidation of the same originating material proceeds under otherwise identical conditions, the oxidation in this second vessel can proceed substantially quicker than—or at least almost as quickly as—it does in the first vessel, although owing to the oxidation in the first vessel, the oxygen content of the air has diminished by the time the air enters the second vessel. The rate of oxidation in the succeeding vessel, or vessels, is thus—owing to the fact that the current of air brings reaction accelerators with it from the preceding vessel—no longer solely dependent—assuming the operation to be conducted under otherwise identical conditions—on the oxygen concentration in the current of air. A lower oxygen concentration of the air can be entirely, or partially, counter-balanced by substances brought by the air, from a reaction vessel

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in which the air has already served for oxidation. If the operation be performed with liquid or solid oxidising agents, and a gas such as nitrogen, carbon dioxide or gases of combustion—or an amount of air insufficient for the oxidation, be passed in succession through the vessels, then provided said vessels are operated under otherwise identical conditions, the reaction proceeds more rapidly in the succeeding vessels than in the preceding ones.

In the oxidation of hydrocarbons of high molecular weight, it has already been proposed to make the working conditions gradually milder while the oxidation proceeds, this being effected for example by allowing the oxidising agent to flow through several oxidation vessels arranged one behind the other, the first of which vessels is charged with the most difficultly oxidisable initial material, while in the subsequent vessels, the already oxidised more sensitive product is exposed to the action of the oxidising gases flowing off from the previous oxidation vessels, the oxidising action of which gases is much milder.

In contradistinction to the foregoing proposal, the present invention provides a process for the production of oxidation products, such as fatty acids or alcohols from hydrocarbons of high molecular weight, by oxidation with gaseous oxidising agents, in which the hydrocarbons are treated, in a plurality of reaction vessels, by passing a current of air or other oxidising gas through the several reaction vessels in succession, and in which additional amounts of air or other oxidising gas are introduced into one or more of the vessels disposed in succession in relation to the flow of the gas.

In the process of the present invention, the rate of reaction increases to the maximum in the vessels supplied with said additional quantities of air or other oxidising gas, and is substantially higher than in those into which the current of air or other oxidising gas is first admitted. The amount of air or oxidising gas admitted into these latter can be reduced by the amount that is subsequently admitted to the other reaction vessels. At the same time, the course of operation in each vessel can be extensively controlled and adjusted by the admission of the additional oxidising gas to the successively disposed vessels. The temperatures can be supervised and adjusted. Known means suffice to prevent frothing-over in any of the vessels, and if necessary, pressure differences between the several vessels can be prevented, for example by employing the oxidising gas, freshly introduced into each vessel, to exhaust the current of gas from the preceding vessel, by such means as an injector. The process according to the invention has the further advantage that oxidation products of a high degree of purity are obtained. This last fact is evidently due to the circumstances that a certain hydrogen-ion concentration—within the slightly acid range—of the interacting substances is beneficial for the production of fatty acids. This acidity of the reaction mixture and the automatically resulting concentration of the accompanying dissociated substances, is favourably maintained by the introduction, primary formation and removal—facilitated by their volatility—of the more readily volatile oxidation products. A probable explanation is that there is established between the reaction products introduced and carried away by the flow of gas and those formed during the oxidation, a state of equilibrium which is precisely most favourable for the oxidation when additional amounts of gas are introduced into the successively disposed vessels, or some of them. Moreover, in contrast to the said known process, the addition of special acids of low molecular weight, acting as catalysts, is dispensed with, and it is therefore superfluous to introduce these continuously, in the anhydrous state, into the process, and, in turn, to separate them in the anhydrous state, from the vapours. Above all, however, by employing a current of air, the present process enables the operation to be performed in such a rational manner that a minimum consumption of air, combined with the most effective utilisation of its contained oxygen, is sufficient.

Since the current of oxidising gas passed through the hydrocarbons to be oxidised is also accompanied by negative catalysts, such as steam, which prevent the course of the reaction from becoming too violent, the present process also offers the advantage of reliably preventing over-oxidation which might, in some circumstances, lead to explosions. The oxidation can also be effected with amounts of oxygen representing a very slight excess—for example 1.2 to 2 times—the amount theoretically required. A further advantage of the process consists in that the loss of material in the gas issuing from the apparatus remains very small. Though it is also possible to keep the losses of sprayed material down to a low level by suitable foam separators, condensers and dephlegmators, they cannot be reduced below a certain amount in each separately operated apparatus. The serial arrangement of the apparatus enables the total losses in the whole plant to be reduced to the amount incurred in a single apparatus. The effect obtained with the present process will be evident from the following experiments:—

EXAMPLE I.

In three equal reaction vessels, connected in series, each charged with 150 litres of the same raw material (paraffin mass produced from hydrogen and carbon monoxide by the Fischer-Tropsch process) and the same small amount of catalyst, viz. 0.3% of manganese stearate with additions of magnesium stearate and synthetic fatty acid, the oxidation was carried out by passing in air, at a temperature of 120 to 125° C. for 36 hours. Additional air was introduced into the second and third vessels, the amount in each case being one-tenth of that admitted into the first vessel. At the end of the said time, the products gave the following acid values:—

In the first vessel -	93
In the second vessel -	111
In the third vessel -	125

The initial boiling point of the three oxidation products—under a pressure of 14 to 16 mm.—was 151 to 157° C. and therefore the higher acid values of the products from the second and third vessels, as compared with those from the first vessel, cannot be ascribed to a content of carried over readily volatilisable acids. Therefore, despite the considerably lower oxygen content of the air carried over into the second or third vessel, the oxidation in the second and third stages has progressed substantially further, under the influence of the volatile products carried over from the preceding vessel than in the first vessel. The admission pressure of the air had to be increased to only a slight degree—in this example from 2 to 2.1 atmospheres (positive pressure) in comparison with apparatus connected in parallel.

Of course, any convenient number of vessels may be employed. In practice, the number can range from about two to twelve. The oxidation itself can be performed, in known manner, under ordinary, slightly reduced or positive pressure. Pressures up to 20 atmospheres (positive) can be employed in practice.

The oxidation can be conducted at temperatures between 60° and 180° C. The actual oxidation temperature selected in each case depends chiefly on the end product desired and on the kind of oxidising agent and catalysts used, the other operative conditions being also suitably adapted. When, for example, aliphatic alcohols are to be produced, it is desirable to keep the reaction medium strongly acid.

It is also important that care should be taken to ensure fine distribution of the gases in the liquid to be oxidised, for which purpose, stirring or mixing devices of various types may be employed. Their effect may also be assisted by the addition of foaming agents, such as Turkey-red oil, and other wetting agents, to the hydrocarbons to be oxidised. In such case, it is advisable to ensure, by the provision of impact surfaces, or other types of baffles, that no foam can be carried over, by the flowing gas, into the succeeding vessel.

In carrying out the invention use will be made of gaseous oxidising agents, such as oxides of nitrogen, more or less pure oxygen, ozone, or preferably air, these being introduced into the liquid, or melted hydrocarbons by means of suitable distributing devices, such as nozzles.

The substances to be chiefly considered as the material to be oxidised comprise: high molecular, saturated or unsaturated, aliphatic hydrocarbons, such as from lamp oil, or "gasol" upwards. Refined tar oils, especially brown-coal tar oils, are also suitable for the process, and brown-coal paraffin forms a highly suitable originating material. Synthetic hydrocarbons such as are formed in the Fischer - Tropsch process, can be employed with particular advantage. Waxy substances, such as montan wax, ozokerite and the like can also be used, and, of course, higher aliphatic hydrocarbons, originating from petroleum, or petroleum products, are also applicable as raw materials for the process.

In order to enable the invention to be more readily understood reference is made to the accompanying drawings, which illustrate diagrammatically and by way of example, two embodiments of apparatus suitable for carrying the same into practical effect, and in which:—

Fig. 1 is a section of an apparatus consisting of three oxidation vessels; and

Fig. 2 is a plan of an apparatus composed of five oxidation vessels.

The reaction vessels 1, 2, 3 shown in Fig. 1 are equipped with gas pipes 4, 5 which, in each case, branch off from the preceding vessel and open into the lower end of the succeeding one. Said pipes may be insulated, to prevent loss of heat, if desired, or provided with additional heating or with cooling means. The vessels are closed and are equipped, for example, with stirrers 6, 7 and 8, together with the requisite heating and cooling devices 9, 10 and 11. The oxidising gas—air for example—is admitted into the vessel 1 through the pipe 12, and issues from the vessel 3 through a pipe 13, which is attached to a condenser 14. Additional oxidising gas is introduced into the vessel 5 through a conduit 5*a*. The pipe 13 discharges into a receiver 15, in which the condensable volatile oxidation products are deposited, whilst the permanent gas passes off through the pipe 16. The stirrers are not indispensable. Moreover—and this is not essential to the invention—the reaction vessels may of course, be of entirely different design, for example horizontal. The admission of the air may also take place, for example through a pipe located in the middle of the apparatus, instead of from below.

In Fig. 2, five reaction vessels 17, 18, 19, 20, 21, are connected in a ring, and interconnected by means of gas pipes 22, 23, 24, 25 and 26, in the same manner as in Fig. 1. In addition, each vessel is equipped with a gas-supply pipe 27, 28, 29, 30 and 31 respectively, and a gas outlet pipe 32, 33, 34, 35 and 36 respectively. These latter can be selectively connected with the condenser 37 and the receiver 38. The vessels and gas pipes may also be equipped with heating, cooling and insulating means, as in the case of Fig. 1.

Apparatus of this kind functions in the following manner: The air is admitted into the vessel 17 through the supply pipe 27 and flows, in succession, through all five reaction vessels charged with hydrocarbons until it is led through the pipe 36 into the condenser 37 and receiver 38. Communication between the vessels is established by the pipes 22, 23, 24 and 25, the pipe 26, gas supply pipes 28, 29, 30, 31 and the gas discharge pipes 32, 33, 34 and 35 being closed. Additional amounts of air are introduced, as required, into the vessels 18, 19, 20, 21, through one or more of the pipes 28, 29, 30, 31, which are correspondingly throttled or, in part, shut off completely. When, after a predetermined reaction period, the oxidation in the vessel 21 is terminated, said vessel is emptied, and re-charged with fresh material to be oxidised. The discharge pipe 36 is then throttled down or closed, as is also the connecting pipe 25 and supply pipe 27 to the vessel 17. Instead of these latter, the supply pipe 31 to the vessel 21, and the discharge pipe 35 on the vessel 20, together with the connecting pipe 26, are opened, and the process is continued until the material in the vessel 20 is completely oxidised. The vessel 20 is then emptied and re-charged and the admission of gas begins from here and passes to the vessel 19, and so on. The process can thus be carried on continuously in a simple manner.

Of course, the reaction vessels can also be superimposed, or otherwise arranged.

EXAMPLE II.

In three successively connected apparatus each of which was charged with 150 litres of paraffin mass, produced from hydrogen and carbon monoxide by the Fischer-Tropsch process, 0.3% of catalyst (manganese stearate, with additions of magnesium stearate and synthetic fatty acids) was added, and the oxidation was conducted with air between 119 and 125° C. All the apparatus were of identical design, viz. vertical, with a simple air nozzle fitted in the conical bottom portion. The air was admitted into the first apparatus, flowing thence through the second and third. Foam separators were provided in the gas outlets of each of the reaction vessels. Fresh air was admitted into apparatus 3, to the extent of one-third the amount flowing through the apparatus 1 and 2. The total amount of air was 1.8 times that needed to supply the oxygen consumed for the oxidation. At the end of 41 hours the acid values were:—

In apparatus 1	147.5
In apparatus 2	147.7
In apparatus 3	160.8

From this it is evident that, in the second apparatus, in which the air contained one-third less oxygen than in the first apparatus, the velocity of the reaction was, nevertheless the same as—and even slightly higher than—the latter, and that, in the third apparatus, the maximum velocity was attained, although in that case, the oxygen content of the air was lower than in the first apparatus, and only a little higher than in the second. The accelerative effect of the flow of gas passing through the apparatus in succession, is therefore very considerable in the succeeding vessels, if gas be also introduced into one or more of the succeeding vessels.

EXAMPLE III.

Three oxidation vessels were each charged with 170 litres of soft paraffin and 450 grms. of a catalyst mixture consisting of fat-soluble, manganese- and sodium compounds. The total amount of compressed air employed was 2.1 times the theoretical air consumption;

the vessel 1 receiving 55% and each of the other two vessels 22.5% of fresh air. Consequently, 55% of the amount of air flowed from the vessel 1 into the vessel 2, and thence mixed with the additional 22.5% into the vessel 3—less the amount of oxygen consumed for the oxidation. After 22 hours, the acid values were:—

In the vessel 1	63
In the vessel 2	76
In the vessel 3	135

The experiment was repeated with the same raw material and catalysers, each vessel being supplied with the same amount of fresh air that was received in the previous case, by the vessel 1. The total amount of air was therefore 1.3 times that in the said case. No air was passed from one vessel to another. The acid values at the end of 22 hours were:—

In vessel 1	68
In vessel 2	65
In vessel 3	72

In the experiment conducted in accordance with the invention, the mean acid value was 91.3, whereas, with separate introduction of air, the mean attained was only 68.3, although the air consumption was greater by one-third.

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). A process for the production of oxidation products, such as fatty acids or alcohols, from hydrocarbons of high molecular weight, by oxidation with gaseous oxidising agents, in which the hydrocarbons are treated, in a plurality of reaction vessels, by passing a current of air or other oxidising gas through the several reaction vessels in succession, and in which additional amounts of air or other oxidising gas are introduced into one or more of the vessels disposed in succession in relation to the flow of the gas.

2). Process as claimed in claim 1, in which, when the several vessels are charged at successive intervals, the current of air or other oxidising gas is first introduced into the vessel which was the last to be charged with the raw material.

3). Process as claimed in claim 1 or 2, in which the passing of the air or other oxidising gas through a plurality of vessels in which different stages of oxidation prevail, is effected in such a manner that said gas passes, in continuous succession, from a vessel the contents of which are in a lower state of oxidation into a vessel with more extensively oxidised contents.

4). Process as claimed in any of claims 1 to 3, in which the material is passed through the successive reaction vessels in the same direction as the current of air or other oxidising gas, but at a slower rate than the latter.

5). The process for the production of oxidation products from hydrocarbons of high molecular weight, substantially as described.

6). Apparatus when used for carrying out the process claimed in the preceding claims, in which a plurality of reaction vessels are detachably connected together, in any convenient serial order by means of gas supply and discharge pipes, a common condenser, or receiver, being preferably provided for collecting the condensable substances from the spent gas.

7). The apparatus when used for the production of oxidation products from hydrocarbons of high molecular weight, constructed, arranged and adapted to operate substantially as described with reference to the accompanying drawings.

Dated this 8th day of June, 1938.

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[This Drawing is a reproduction of the Original on a reduced scale.]

Fig. 1

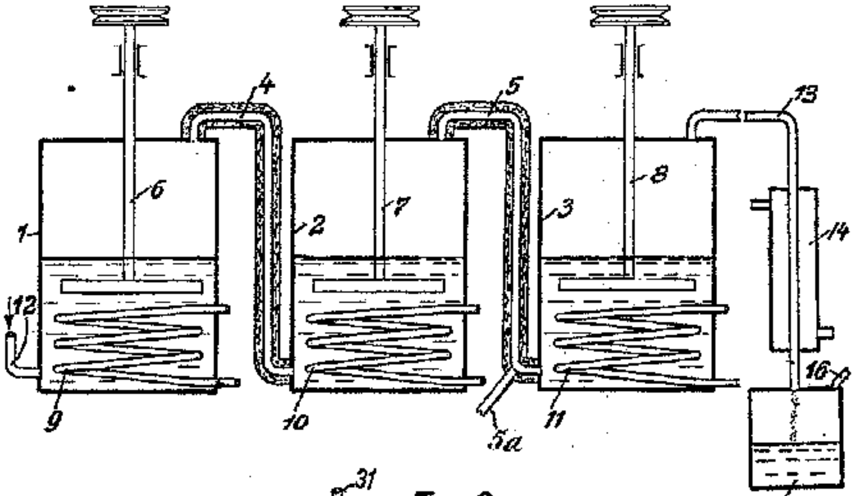
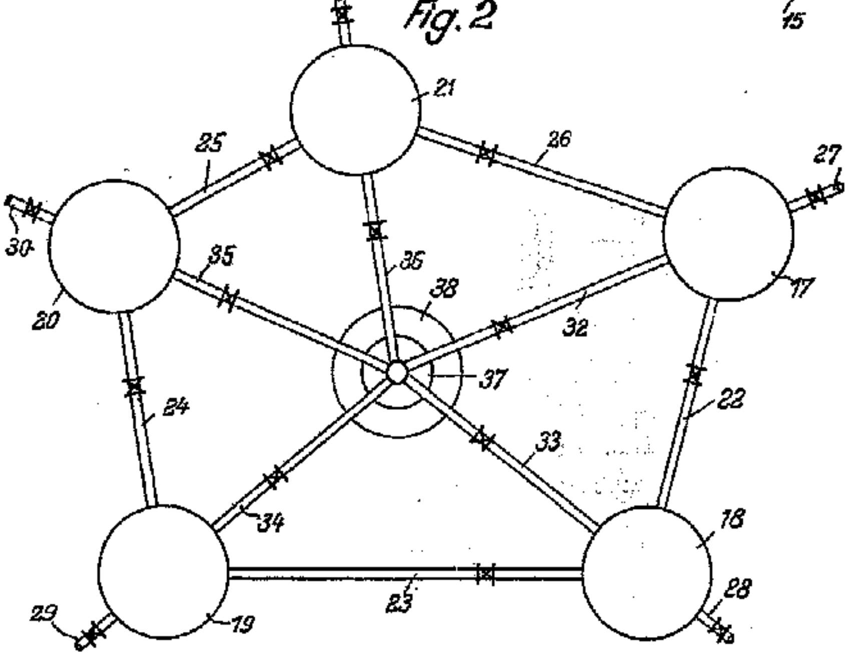


Fig. 2



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