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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Production of Fatty Acids by Oxidation of Paraffin Hydrocarbons

We, 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, and KARL BLASS, a German Citizen, of 1, Oldenstädter Chaussee, Magdeburg, Germany, 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 for the production of fatty acids by oxidation of paraffin hydrocarbons which are liquid under the conditions of treatment.

In the oxidation of aliphatic hydrocarbons to fatty acids, manganese salts have chiefly been proposed as catalysts. According to other methods the elements of the eighth group are employed as catalysts. It has further been proposed to perform the oxidation in the presence of alkalis or of mixtures of compounds of the alkali and alkaline earth metals, including magnesium, on the one hand, and compounds of the earth or heavy metals on the other hand. In accordance with another proposal acids, such as oleic acid, naphthenic acid or the oxidation product of paraffin, are employed as catalyst. Moreover processes for the oxidation of organic compounds have been proposed in which the catalysts are added to the substance to be oxidised in small portions during the course of the oxidation.

In contradistinction to the foregoing proposals, an improvement of the oxidation process is obtained in accordance with the present invention, by employing as catalyst a mixture of free higher carboxylic acids particularly fatty acids, resinic acids and naphthenic acids, and compounds of the metals of the sixth, seventh or eighth group of the periodic table and by adding only a part of the catalyst mixture to the originating material before the commencement of the oxidation treatment, the remainder of the catalyst being added during the course of the reaction. Compounds of the alkali or alkaline earth metals, including magnesium, may also be added to this mixture. These additions are particularly effective if they are employed in the form of salts of the fatty acids or resinic acids, carbonates or bicarbonates, or mixtures of these substances.

Natural fatty acids, resinic acids, or the like, preferably in pure form, or synthetic fatty acids or the like, for example distillation fractions of the synthetic fatty acids or also residues of the distillation of synthetic or natural fatty acids, provided that such residues still contain free or lactonised fatty acids, may be utilised as organic acids of higher molecular weight. Mixtures of these substances may naturally also be used. Salts of the fatty acids, resinic acids or naphthenic acids, for example manganese stearate, cobalt resinate, iron naphthenate, or mixtures thereof, may advantageously be employed as compounds of the metals of the sixth, seventh or eighth group. However, it is also possible to add these metals in the form of inorganic compounds, for example, in the form of iron chloride. Through the simultaneous presence of the above mentioned acids and metal compounds in the catalyst of the present invention, the unexpected result is obtained that the reaction starts immediately the reaction temperature is reached, even when working with large charges, and that the formation of oxy-acids insoluble in petroleum ether and of oxy-fatty acids is very extensively suppressed. The reaction takes place in a fraction of the time that is required in the case of the known use of higher carboxylic acids as catalysts. In addition, despite the use of small amounts of catalysts, the requirements of oxygen or air are very small, since only about twice the theoretical amount is sufficient, particularly when a current of gas is passed through a plurality of reaction vessels one after the other. The most favourable oxidation temperatures lie between about 90 and 150° C.

The oxidation can take place for

example in vessels equipped with stirrers, the blades (provided with apertures) of the stirrers alternately cutting through the layers of gas and liquid in rapid succession. Other devices may also be used which likewise permit thorough mixing of the liquid with the gas.

In carrying out the invention a large proportion, i.e. about one to two thirds, of the total amount of catalyst is preferably added to the material to be oxidised before the commencement of the reaction. The remainder may be added at a later stage of the process, either all at once or in smaller partial amounts at different times or continuously. As a rule it is sufficient to divide the catalyst into two portions and to add the second portion, for example, after attaining an acid number between about 60 and 120, preferably before the material turns a dark colour. When the catalyst is added in smaller partial amounts, for example at intervals of about two or three hours, or when the remainder of the catalyst is added continuously, the oxidation process can be so conducted that the increase in the acid numbers or saponification numbers remains practically constant throughout the duration of the oxidation up to the desired stage of oxidation. A retardation then occurs only when the content of fatty acids and saponifiable substances attains about 90% of the material. In addition, the material remains very light and displays no tendency to resinify. By admixing the catalyst in a plurality of stages, it is thus possible to suppress the formation of oxyacids and oxy-fatty acids and their tendency towards polymerisation very extensively.

It has further been found that, when using the mixed catalyst of the aforedescribed composition, it is also possible to conduct the reaction further up to a 90% and higher conversion into fatty acids, if the partial amounts of catalyst added during the course of the reaction consist merely of compounds of the metals of the sixth, seventh or eighth groups of the periodic table, or mixtures of these substances, or mixtures of these substances with alkali metal, alkaline earth metal or magnesium compounds. It is thus sufficient that the portion of catalyst added before the commencement of the reaction, which must be made correspondingly large, should contain an addition of fatty resinic or naphthenic acids in accordance with the invention. The fatty acids formed in the first stage of the oxidation then also effect the desired acceleration during the further course of the oxidation, in conjunction with the above mentioned subsequently added portions of catalyst, whereas by adding at the beginning of the reaction a catalyst mixture containing no free higher molecular acids, only a relatively slow oxidation is produced, so that it is impossible to conduct the reaction up to a content of 90% of fatty acids, in consequence of resinification occurring at an early stage.

In order to obtain the best results it is thus important to make the portion of catalyst added before the commencement of the reaction sufficiently large, particularly as regards the content of free higher molecular organic acids. When using those apparatus which permit intensive mixing between, for example, compressed air and oxidation material, it is preferable to work with about twice to four times the theoretical amount of air.

The amount of catalyst employed is generally somewhere between 0.1 and 1.5% of the hydrocarbon material. The minimum amount required for a determined originating material is preferably determined by a preliminary trial.

Manganese stearate, manganese palmitate, manganese oxalate, corresponding cobalt compounds, magnesium stearate, or else inorganic compounds, such as manganese chloride, iron chloride, bichromates, uranium nitrate, sodium carbonate and the like, and also stearic acid, linoleic acid and other high molecular fatty or resinic acids may be used, for example, as components of the catalyst mixture. A particularly suitable mixed catalyst consists, for example, of from 3 to 6 parts of manganese stearate, 1 to 3 parts of magnesium stearate, 1 to 2 parts of sodium or other alkali metal bicarbonate, and 1 to 3 parts of stearic acid or synthetic higher molecular fatty acids. As already mentioned, the amount of free acid contained in the portions of catalyst added during the course of the oxidation can be reduced, or be dispensed with altogether. It has transpired, however, that an addition of alkali metal compounds alone, for example, at a later stage of the process is no longer able to accelerate or re-start the reaction, while an addition of a mixture of, for example, manganese stearate and iron chloride at the same stage produces such a violent reaction that a rapid increase in the acid numbers is obtained and the cooling, or withdrawal of the heat of reaction, must be correspondingly intensified.

Whereas, when the whole amount of

the catalyst is added before the commencement of the oxidation, a discoloration and resinification of the oxidation products may already occur when their content of fatty acids has risen to about 75% during the course of the oxidation, there is obtained by adding the catalyst a portion at a time if the oxidation is interrupted at this content of about 75% of fatty acids, a product which is distinguished by an extremely low content of oxyacids insoluble in petroleum ether, oxy-fatty acids, and the like. This feature of the invention thus makes it possible to obtain relatively pure products by thus interrupting the oxidation at fatty acid contents in the oxidation products of about 70 to 80%. However, if such pure products are not required, the oxidation may be conducted very extensively up to contents of over 90% of oxidised substances, which could not hitherto be obtained in practical operation.

In connection with the use of other catalysts or of oxidation methods working with oxides of nitrogen it has already been proposed to break off the oxidation prematurely in order to reduce the undesirable by-products in the final product.

However the process of the present invention, by virtue of the use of a mixed catalyst containing free higher carboxylic acids and the addition of such catalyst in partial amounts, in a manner known per se, enables the oxidation to be conducted up to a content of 90 to 95% of fatty acids, or when the oxidation is prematurely broken off, a substantially purer product to be obtained than was possible by known methods.

A further advantage of the process consists in that, when the catalyst is added in partial amounts, it is possible to work at a reaction temperature lying far below the reaction temperature required when it is added all at one time. For example, it is possible to maintain reaction temperatures of 95° C. and lower without difficulty, accompanied by a rapid increase in the oxidation, and thus to suppress still further side reactions, such as the formation of oxyacids.

The non-oxidised residue of the originating substance—the unsaponifiable portion—may be subjected, after separation from the fatty acids produced, to further oxidation, which is preferably carried out by the process of the invention. When this material is oxidised by the present process the afore-described advantages are similarly obtained. Since the production of fatty acids by oxidation of paraffinic hydrocarbons is above all rendered expensive and bothersome by the necessary separation of the unsaponifiable substances, simplification and economy result from working in accordance with the invention, since even by a single oxidation a pure and high grade product is obtained, from which only comparatively small fractions have to be separated and, if desired, further oxidised.

EXAMPLE I.

150 kgs. of paraffin crudes, obtained in the production of hydrocarbons by catalytic conversion of hydrogen and carbon monoxide by the Fischer-Tropsch synthesis, were treated at an oxidation temperature of 120° C. with a mixed catalyst consisting of 78.5% of fat-soluble manganese, magnesium and alkali metal compounds, and 21.5% of stearic acid.

Before the commencement of the reaction only the stearic acid and 48% of the fat-soluble metal compounds were added. The remainder of the fat-soluble catalysts were added after 12 hours. After 27 hours the acid number was 175.3.

EXAMPLE II.

150 kgs. of paraffin crudes, boiling above 320° C. were mixed at the beginning with a mixture consisting of one-third soluble manganese compound and two-thirds higher fatty acids. The total accelerator quantity amounted to 0.23% at the commencement. In the course of the oxidation a further 0.4% of catalyst was added, in eight partial amounts. Six of these partial amounts consisted of alternate doses of alkali and heavy metal compounds. The last two were oil-soluble mixtures of the metals of the sixth to eighth group of the periodic table. After the first six hours it was possible to keep the reaction temperature constantly below 110° C. and after addition of the oil-soluble compounds of the sixth to eighth group it was possible to depress the temperature to 93.5° C. Nevertheless, the increase of the acid number within three hours was on the average 15. In 38 hours an acid number of 159.2 was attained. The oxidised material was almost colourless.

The heavy metal compounds consisted of manganese, iron and cobalt salts in the proportion of one-fifth iron salts and four-fifths manganese and cobalt salts in equal parts. The salts were mixtures of chlorides and carbonates in the proportion of 1:1.

EXAMPLE III.

The same quantity of crude paraffin was oxidised at 125° C. with air. After

26 hours the yield of fatty acids was 92.5%.

Manganese palmitate was used as catalyst, 45.5% of the quantity of total manganese palmitate employed being first added in admixture with the same amount of stearic acid, while the rest was added without admixture of stearic acid or the like in two doses of 27.25% each in the course of the oxidation.

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

1). A process for the production of fatty acids by catalytic oxidation of paraffin hydrocarbons which are liquid under the conditions of treatment, in which salts of the metals of the sixth, seventh or eighth group of the periodic system are used as catalysts together with free higher carboxylic acids such as fatty, resinic or naphthenic acids, if desired with the addition of compounds of the alkali or alkaline earth metals including magnesium, and in which only a part of the catalyst mixture is added to the originating material before the commencement of the oxidation treatment, and the rest of the catalyst is added during the course of the reaction.

2). Process as claimed in claim 1, in which the amount of the catalyst added before the commencement of the reaction is about from one-third to two-thirds, preferably 50 to 70% of the total amount of catalyst employed.

3). Process as claimed in claims 1 and 2, in which only the catalyst mixture added before or at the commencement of the reaction contains free higher carboxylic acid, while in later stages of the reaction compounds of the metals of the sixth to eighth groups, or mixtures thereof with alkali metal, alkaline earth metal or magnesium compounds, are added.

4). Process as claimed in claims 1 to 3, in which the remainder of the amount of catalyst is added continuously after initiation of the reaction.

5). Process as claimed in claims 1 to 4, in which the partial amounts of catalyst are added in such a way that the increase of the acid number within equal periods remains approximately constant throughout the whole process.

6). Process as claimed in claims 1 to 5, in which the oxidation is prematurely broken off.

7). Process as claimed in claims 1 to 6, in which the process is carried out under very mild oxidation conditions below a temperature of 120° C.

8). The process for the production of fatty acids by the catalytic oxidation of paraffin hydrocarbons, substantially as described.

Dated this 4th day of May, 1938.

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