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PROCESS FOR THE MANUFACTURE OF BORATE ESTERS OF LONG CHAIN ALIPHATIC ALCOHOLS

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ABSTRACT OF THE DISCLOSURE

Borate esters of long-chain aliphatic alcohol are prepared by the oxidation of paraffins containing from 10 to 20 carbons in the presence of boric acid and its dehydration products, as catalysts and esterification components, by adding to the paraffin, preheated to at least about 170° C., 5 to 10% of ortho-boric acid and rapidly dissolving it with extensive dehydration, oxidizing by introducing a gas mixture containing oxygen and then completing the oxidation at a reduced temperature.

After separation of unreacted paraffins, the borate esters can be hydrolyzed to the corresponding alcohols.

The present invention relates to a porcess for the manufacture of long chain aliphatic alcohols by oxidation of unbranched paraffins in the presence of boric acid or of dehydration products thereof.

It is known from German Patent 552,886 that solid or liquid hydrocarbons can be oxidized in the liquid phase at temperatures in the range of from 160 to 200° C. in the presence of boric acid, a mixture of boric acid and acetic acid or the anhydrides of these acids, with oxygen or with oxygen-containing gases. In this process, the boric acid or the anhydro-products thereof are not only catalysts in the conventional meaning, but they represent at the same time an intercepting agent. The quantity of boric acid namely is adjusted in such a manner that the alcohols formed during oxidation are bound in the form of borates and are thus no longer exposed to the oxidizing action of the oxygen.

In this oxidation, however, ketones or acids are formed to a lesser or greater extent as undesired byproducts. Thus, as it is stated in German Patent 552,886, the yield of alcohols depends essentially on the period of oxidation and on the conditions of this oxidation. If the treatment with oxygen is effected for too long a period and too high a temperature, the formation of ketones and acids is increased at the loss of the alcohols; if, on the other hand, the oxidation period is too short and the temperature too low, the yield of alcohol is better, but the reaction rate is too low. Therefore, the oxidation is effected in a very narrow temperature range, i.e. at temperature in the range of from 165 to 175° C., as results from the examples of said patent. Hence, this process is economical in

this very narrow temperature interval and the formation of undesired byproducts is limited.

On the other hand, British Patent 353,047 expressely states that even in this temperature range the oxidation sets in noticeably no sooner than after one hour, thus that the boric acid must first be activated during this time. Thus, the initially poor reaction rate is tolerated in favour of a decomposition, which takes place preferably at this temperature range, of the primarily formed hydroperoxide in direction towards alcohols, since at the same time at least the formation of undesired ketones and acids remains low. A further lowering of the reaction temperature seems not to be possible in view of the obtainable reaction rate disclosed in French Patent 1,359,064, since in this patent, there is stated in Example 6, as comparison to Example 1, that at 130° C. no reaction could be observed. These facts can be explained only by assuming that the catalysts used for the conversion of paraffin hydrocarbons into fat alcohols, in this special case the boric acid, are only very sparingly soluble in the hydrocarbons, depending on the manner of adding them, and that upon the dehydration which takes place during heating of the reaction mixture, they are not homogeneously distributed in this mixture despite intensive mixing with the aid of an inert gas and that they adher to a lesser or greater extent to the wall of the reaction vessel. If, in the course of the following oxidation in the indicated temperature range and at least partial dissolution of the boric acid is enforced and thus the oxidation is running fully, the prolonged treatment with oxygen at temperatures in the range of from 165–175° C. is necessary to obtain an economical reaction rate. However, owing to the prolonged reaction period at elevated tempearture, the formation of undesired byproducts is also increased.

French Patent 1,166,679 attempts to by-pass this inconvenience by proposing as catalysts, instead of boric acid, phosphorous acid or arsenious acid, the esters of these acids which are better soluble in paraffin. The use of these esters, however, involves also the use of more complicated apparatus, because, in addition to the additional preparation of these esters, the lower alcohols liberated during the reaction by transesterification must also be recovered.

Now, we have found that, surprisingly, long-chain aliphatic alcohols can be prepared by the oxidation of paraffins containing from 10 to 25, preferably 12 to 15, carbon atoms, in the presence of boric acid and its dehydration products as catalysts and esterification components, and separation of unreacted paraffins and hydrolysis of the resulting borates, by adding to the paraffin preheated to at least 170° C. 5 to10% by weight, preferably about 5 to about 6% by weight, referred to the paraffin, of orthoboric acid and rapidly dissolving it with extensive dehydration, effecting the oxidation at the temperature defined above by introducing a gas mixture containing oxygen and allowing the oxidation to complete at a reduced temperature in the range of about 130 to about 165° C. The induction period after dissolution of the boric acid is about 5 to about 45 minutes, preferably 15–30 minutes. As the oxidizing agent, a gas mixture consisting of nitrogen and about 2 to about 10% by volume of oxygen, preferably about 4 to about 5% by volume of oxygen, is used in amounts of about 400 litres/hour/kg. of paraffin.

In the process of the present invention, it was surprising that the above-described disadvantages, i.e. poor reaction rate with high alcohol yield or good reaction rate with poor alcohol yield, could be avoided by subjecting the ortho-boric acid used as the catalyst and esterification component to a certain treatment. It has been found that ortho-boric acid in the quantity required for a maximum reaction of about 35% for the conversion of the alcohols formed into the corresponding borates is almost completely soluble in the paraffin with simultaneous dehydration, if this acid is introduced at a temperature above its melting temperature, preferably at temperatures above 175° C., into the correspondingly heated paraffin.

In contradistinction to the method hitherto used, wherein mixtures of paraffin and boric acid are heated whereby undesired agglomerations are formed, the process of the present invention permits homogeneous dissolution of the dehydrated boric acid in the paraffin. Owing to the elevated temperature applied during the addition, the hitherto required removal by means of a stream of nitrogen of the water formed by the dehydration of ortho-boric acid is not necessary. By this dissolution effect, the boric acid is activated to such a degree that the oxidation sets in immediately upon introduction of the gas containing oxygen, which can be seen from the decrease of the oxygen content of the residual gas. The activation of the dehydrated and dissolved boric acid is sufficient to permit carrying out the main reaction in a temperature range of from 150 to 155° C., after corresponding reduction of the reaction temperature, without the reaction rate being decreased or the reaction time being increased. The activation of the dehydrated and dissolved ortho-boric acid is advantageously increased during a short induction period at the temperature at which the addition is carried out, by introducing oxygen-containing gases and then reducing the reaction tempearture to 150–155° C.

Owing to the presence of large quantities of dissolved dehydrated boric acid in activated form, a high reaction rate is obtained in almost the same time with an alcohol yield of 85 to 87%, with only a small formation of ketones and acids, despite the more moderate reaction conditions, which has not been obtained as yet. Even at a temperature of 130° C., it was possible to obtain with a catalyst activated in such manner a reaction rate of 12%, in contradistinction to the reaction rate obtained according to the above-mentioned French patent.

Another advantage of the process of the present invention is that the products obtained are practically colorless, whereas the oxidation products obtained at a higher reaction temperature show a distinct yellow color.

The secondary alcohols thus obtained serve for the preparation of surface-active compounds, especially as starting materials in the preparation of detergents, which are biologically easily decomposable.

The following examples illustrate the invention but they are not intended to limit it thereto:

EXAMPLE 1

200 g. of tridecane are filled into a glass frit tube having a ratio of length of diameter of 20:1 to 10:1, which is provided at its bottom with a filter plate through which oxygen diluted with nitrogen is introduced, and at its head with a cooler with water separator, and which is furthermore provided with an external, heatable jacket, and the tridecane is heated to a temperature in the range of 175–180° C. In order to secure uniform heating of the paraffin hydrocarbon, a stream of nitrogen may be passed through the reaction tube during heating. When the above-mentioned temperature is reached, 12 g. of ortho-boric acid (6% by weight, referred to the tridecane used) are added portionwise. The ortho-boric acid dissolves homogeneously, under dehydration and simultaneous foaming, in the tridecane. If large single portions are added, it may

be that a small residue of undissolved and only partially dehydrated boric acid accumulates on the filter plate, but this residue passes also in solution during the reaction.

As soon as the addition of ortho-boric acid is complete, a mixture of nitrogen and oxygen, containing 5% of oxygen, is passed with a speed of 60 to 80 l./h. through the homogeneous solution of tridecane and dehydrated ortho-boric acid. Oxidation sets in immediately, which can be seen within a few minutes from the decrease of oxygen content of the residual gas. During this time, any small amounts of dehydrated boric acid which have accumulated on the filter plate also pass into solution.

About 30 minutes after the beginning of the introduction of the nitrogen/oxygen mixture, the reaction mixture is cooled to a temperature in the range of 150 to 155° C. and then treated at this temperature for 3½ hours with the same gas mixture and at the same introduction speed.

During the total period of reaction, the vapors formed are continuously eliminated from the reaction vessel and condensed. After separation, the water is rejected, while the tridecane is recycled into the reaction zone.

When the reaction is complete, the colorless reaction product is worked up in known manner by distillation under reduced pressure, 144 g. of unreacted trideane are separated, which correspond to a reaction rate of about 28%. As residue, there remain borates of the tridecanols formed by the reaction and other oxidation products which are subsequently mixed, while stirring vigorously, with 250 g. of water and heated for 1 hour to 80° C. The borates are thereby hydrolized. The organic phase which separates during hydrolysis is separated and washed with a small amount of water. 59 grams of a product are obtained which contains, according to analysis, about 87% of tridecanols, 5% of tridecanone and, as to the remainder, other oxidation products.

Compared thereto, the reaction rate with non-activated boric acid, the same reaction temperature of 155° C. and for the same period of time, amounts to 9% only. With the same catalyst, at 175° C., the reaction rate is higher, but the yield of alcohol is then about 50 to 60% only.

EXAMPLE 2

12 g. of ortho-boric acid are dehydrated as described in Example 1 at 175–180° C., in 200 g. of pentadecane, and dissolved and then activated in the course of half an hour in the presence of oxygen. Oxidation is then continued at a temperature reduced to 130° C. After working up of the reaction product, it has been found that about 12% of the paraffin used initially have been reacted, whereas it is stated in Example 6 of French Patent 1,359,064, that at 130° C., under the conditions described in said example, no reaction takes place.

We claim:

1. In the preparation of borate esters of long chain aliphatic alcohols by the oxidation of paraffins containing from 10 to 25 carbon atoms, the improvement which comprises preheating the paraffin to at least 170° C., admixing about 5 to 10% by weight, referred to the paraffin, of ortho-boric acid to effect solution thereof, effecting the oxidation at a temperature in the range of about 170 to about 175° C. for an induction period by introducing a gas mixture containing oxygen and thereafter completing the oxidation at about 130 to about 165° C.

2. A process as claimed in claim **1**, wherein the paraffins contain 12 to 15 carbon atoms.

3. A process as claimed in claim **1**, wherein about 5 to about 6% by weight, referred to the paraffin, of ortho-boric acid are used.

4. A process of claimed in claim **1**, wherein a gas mixture consisting of about 90 to about 98% by volume of nitrogen and about 10 to about 2% by volume of oxygen, is used in an amount of about 400 l./h./kg. of paraffin.

5. A process as claimed in claim **4**, wherein a gas mixture consisting of about 95 to about 96% by volume of nitrogen and about 5 to about 4% by volume of oxygen, is used.

6. A process as claimed in claim **1**, wherein after the dissolution of the boric acid, the induction period is about 5 to about 45 minutes.

7. A process as claimed in claim **6**, wherein the induction period takes about 15 to about 30 minutes.

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