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PROCESS

The present invention relates to a process for preparing organic hydroperoxides and to processes in which such organic hydroperoxides are used, such as the preparation of oxirane compounds and preparation of alkenyl aryl compound.

Background of the invention

Processes for preparing propylene oxide employing organic hydroperoxides, are well known in the art. As described in US-A-5,883,268, such process conventionally comprises peroxidation of ethylbenzene, followed by contacting the peroxidation reaction product with aqueous base in amount sufficient to neutralize acidic components thereof and separating the resulting mixture into an aqueous stream and a deacidified organic stream. The base contaminated, deacidified hydroperoxide stream is washed with water and the resulting mixture separated into an organics contaminated water phase and an organic phase having a reduced alkali metal content.

Surprisingly, it was found that the amount of contaminants in the organic hydroperoxide finally obtained, can be reduced further in a simple and effective way.

Summary of the invention

The present invention relates to a process for preparing organic hydroperoxides, which process comprises:

- (a) oxidation of an organic compound to obtain reaction product containing organic hydroperoxide,
- (b) treating at least part of the organic hydroperoxide containing reaction product with a basic aqueous solution

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and separating hydrocarbonaceous phase containing organic hydroperoxide from basic aqueous phase,

(c) washing with water at least part of the separated hydrocarbonaceous phase containing organic hydroperoxide
5 and separating hydrocarbonaceous phase containing organic hydroperoxide from aqueous phase, and

(d) optionally repeating step (c) one or more times, in which process solid particles are removed from the reaction product containing organic hydroperoxide and/or
10 basic aqueous solution before use in step (b).

Preferably, the solid particles are removed by filtering at least part of the reaction product containing organic hydroperoxide and/or at least part of the basic aqueous solution before use in step (b).

15 The gist of the present invention resides in the fact that solid particles are removed from at least part of one or more of the feed streams before these feed streams are used in step (b). The feed streams which are subjected to process step (b) are the organic
20 hydroperoxide containing reaction product obtained in step (a) and the basic aqueous solution with which the organic hydroperoxide containing reaction product is treated.

25 It was observed that in conventional operation, an interface emulsion layer or rag could form upon washing the hydrocarbonaceous phase containing organic hydroperoxide. Such layer can cause an increased amount of basic aqueous solution in the organic phase. The presence of a substantial amount of basic aqueous
30 solution in the organic phase tends to cause problems in the further processing of the organic hydroperoxide mainly caused by the presence of basic compounds, more specifically compounds such as sodium hydroxide and calcium hydroxide.

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Organic hydroperoxides are useful in a range of processes. One of these processes is the reaction of organic hydroperoxide with olefin in order to obtain oxirane compounds. In such process, the organic compound usually is an alkylaryl compound, and the process further comprises:

- (e) contacting at least part of the hydrocarbonaceous phase containing alkylaryl hydroperoxide obtained in step (c) and/or (d) with olefin and catalyst to obtain alkylaryl hydroxide and oxirane compounds, and
- (f) separating at least part of the oxirane compound from the alkylaryl hydroxide.

The alkylaryl hydroxide obtained in step (f) can be used in a wide range of processes. Such process is preparing an alkenyl aryl compound by dehydrating the alkylaryl hydroxide. Another process is hydrogenating the alkylaryl hydroxide to obtain an alkylaryl compound. If the process according to the present invention is to be used for dehydrating the alkylaryl hydroxide, the process suitably comprises further:

- (g) converting at least part of the alkylaryl hydroxide obtained in step (f).

Preferably, step (g) comprises either dehydration or hydrogenolysis of the reaction product. Hydrogenolysis is the reaction of the alkylaryl hydroxide with hydrogen, preferably in the presence of catalyst. Dehydration will generally produce an alkenyl aryl compound and water, while hydrogenolysis will generally produce alkylaryl compound. Preferably, the hydrogenolysis will produce the alkylaryl compound used as starting compound.

Detailed description of the invention

Although the organic compound used in the process of the present invention can in principle be any compound, organic compounds which are most frequently used are alkylaryl compounds, more specifically benzene compounds

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containing at least 1 alkyl substituent which alkyl substituent contains of from 1 to 10 carbon atoms, preferably of from 2 to 8 carbon atoms. Preferably, the benzene compound contains on average of from 1 to 2 constituents. The alkylaryl compounds most frequently encountered are ethylbenzene, cumene and di(iso-propyl)benzene.

The oxidation of the organic compound can be carried out by any suitable process known in the art. The oxidation can be carried out in the liquid phase in the presence of a diluent. This diluent is preferably a compound which is liquid under the reaction conditions and does not react with the starting materials and product obtained. However, the diluent can also be a compound necessarily present during the reaction. For example, if the alkylaryl compound is ethylbenzene the diluent can be ethylbenzene as well.

Besides the desired organic hydroperoxide, a wide range of contaminants are created during the oxidation of organic compounds. Although most of these are present in small amounts, the presence of the organic acids especially has been found to sometimes cause problems in the further use of the organic hydroperoxides. As described in US-A-5,883,268, a method of reducing the amount of contaminants is contacting the reaction product containing organic hydroperoxide with an aqueous alkali solution. However, contact with the aqueous alkali solution introduces a certain amount of alkali metal into the organic hydroperoxide containing reaction product. The amount of organic acids is decreased by an alkali wash but the amount of alkali metal contaminants is increased.

In the process of the present invention, the organic hydroperoxide containing reaction product is contacted with a basic aqueous solution, more specifically a basic

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aqueous solution containing one or more alkali metal compounds. Suitable alkali sources for use in the aqueous alkali solution include alkali metal hydroxides, alkali metal carbonates and alkali metal hydrogen carbonates. Examples of these compounds are NaOH, KOH, Na₂CO₃, K₂CO₃, NaHCO₃ and KHCO₃. In view of their easy availability, it is preferred to use NaOH and/or Na₂CO₃.

The basic aqueous solution preferably contains fresh basic aqueous solution, recycled basic aqueous solution and optionally additional water. The recycled basic aqueous solution has been obtained from step (b).

The exact conditions under which step (b) is carried out, strongly depend on the further circumstances. Preferably, step (b) is carried out at a temperature of between 0 °C and 150 °C, more preferably of between 20 °C and 100 °C.

In step (b), the hydrocarbonaceous phase is subsequently separated from the aqueous phase. A preferred method comprises allowing the hydrocarbonaceous phase and aqueous phase to settle in a settling vessel and subsequently separating a hydrocarbonaceous phase from an aqueous phase. Preferably, the hydrocarbonaceous phase containing organic hydroperoxide is subsequently sent to a coalescer where further aqueous phase is removed. Preferably, the separation is carried out at a temperature of between 0 °C and 150 °C, more preferably of between 20 °C and 100 °C.

In conventional operation, an interface emulsion layer or rag was sometimes observed upon washing the hydrocarbonaceous phase containing organic hydroperoxide. Surprisingly, it has now been found that such rag formation could be prevented by removing solid particles from one or more of the feed streams used in step (b). Without wishing to be bound to any theory, it is thought that the rag formation was due to the presence of solid

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particles, such as small, insoluble particles of metal compounds such as iron. Such metal compounds can be formed in the corrosion of metal surfaces. The organic hydroperoxide containing reaction product could pick up such metal compounds during oxidation. Furthermore, the stream containing the organic compound can already contain such solid particles before the oxidation. The basic aqueous solution could pick up such metal compounds from recycled basic aqueous solution and/or from waste water which is used in the preparation of the basic aqueous solution. Both feed streams can pick up metal compounds during storage. Solid particles can be removed in different ways. Solid particles can be removed in any way known to someone skilled in the art. Suitable methods comprise treating at least part of one or more of the feed streams used in step (b) with an ion exchange resin, with an adsorbent and/or filtering at least part of these feed streams. It was found that filtering was the preferred method of removing solid particles.

The temperature and pressure at which the filtering can be carried out, are well known to someone skilled in the art and depend on the compounds present.

The filter which is preferably used for filtering the feed streams of step (b) has openings of 50 micrometres or less, preferably 30 micrometres or less, more preferably 20 micrometres or less.

The filter can be made of any material which is known to be suitable by someone skilled in the art. Filters made of polypropylene and cellulose were found to perform well. It is well known that the filters will slowly plug which is shown by an increased pressure drop over the filter. When the pressure drop becomes too high, the filter can be taken out of operation, cleaned and be returned as will be well known to someone skilled in the art. Alternatively, the filter can be cleaned by feeding

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a clean liquid such as cumene or ethylbenzene in the reverse direction of the normal flow, so-called back-flushing. The latter has the advantage that the filter does not need to be removed.

5 As mentioned above, each of the feed streams which is used in step (b) can contain metal compounds which need to be removed. The amount of metal compounds which is incorporated in the organic hydroperoxide containing reaction product produced in step (a) depends on the
10 amount of metal compounds present in the organic compound subjected to step (a) and on the exact processing conditions in step (a). The amount and kind of metal compounds present in step (a) will determine whether solid particles need to be removed from the product of
15 step (a), or part of it.

 The basic aqueous solution used in step (b) can pick up metal compounds from various sources. The amount of metal compounds present in each source, will determine when solid particles are preferably removed from the
20 basic aqueous phase.

 In order to further improve the separation of aqueous phase and hydrocarbonaceous phase in steps (b), (c) and/or optional step (d), additional compounds can be present. Examples of such additional compounds are so-called emulsion breakers or de-hazers such as aliphatic
25 or cyclic amines.

 In the present description of the invention, the expression water is used to indicate both clean water and waste water which can contain contaminants. If clean
30 water is to be used, this is mentioned separately. The washing with water of steps (c) and (d) can be carried out with clean water and/or waste water.

 It was recently found that the use of waste water, optionally in combination with clean water, has many
35 advantages. This has been described extensively in not-

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prepublished patent application PCT/EP02/10519 (our TS 1068). Therefore, the washing with water of steps (c) and/or (d) preferably is carried out with waste water optionally in combination with clean water.

5 The waste water can be added to separated hydrocarbonaceous phase at any stage. A preferred, specific embodiment comprises adding waste water or aqueous solution containing waste water to a coalescer.

10 Preferably, the water used in step (c) and/or (d) comprises both waste water previously used in washing a hydrocarbonaceous phase containing organic hydroperoxide and a different kind of waste water.

15 The waste water previously used in washing a hydrocarbonaceous phase containing organic hydroperoxide, preferably is a waste water obtained by contacting a hydrocarbonaceous phase containing organic hydroperoxide with an aqueous phase, preferably clean water, and subsequently separating the aqueous phase from the hydrocarbonaceous phase. The aqueous phase so obtained is
20 preferably used as waste water without further treatment. Most preferably, the waste water obtained in this way is used in combination with a different kind of waste water.

25 The washing of the hydrocarbonaceous phase is preferably carried out by contacting the hydrocarbonaceous phase countercurrently with water. Countercurrent operation is considered to comprise contacting with relatively clean water hydrocarbonaceous phase which has already been washed once or more, while contacting hydrocarbonaceous phase which has not yet been
30 washed, with aqueous phase which already has been in contact with hydrocarbonaceous phase.

35 The source of waste water is in principle irrelevant to the present process. However, it is preferred that the waste water is obtained in a process step related to the present process as this reduces the risk that the

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compounds present in the hydrocarbonaceous phase react with those present in the aqueous solution. Furthermore, it is preferred not to introduce new components into the process. It is surprising that the use of waste water gives good results as the aim of the previous process steps was to remove organic acids which were formed as by-products in the oxidation of step (a). It has now been found that waste water can be used in the aqueous wash of step (c) and/or (d), giving good results without negative impact on a subsequent catalyst such as an epoxidation catalyst such as described in EP-A-345856.

Waste water which has been found especially suitable for use in aqueous solutions for the present invention, is waste water which is acidic. Preferably, the acidic waste water comprises one or more organic acids. Organic acids have been found to be generally compatible with the compounds further used in the present process. It has been found especially preferred if the acid which is present is a an organic acid comprising of from 1 to 20 carbon atoms. Preferred organic acids to be present in the waste water include hydrocarbyl carboxylic acids having in total from 1 to 10 carbon atoms. Especially preferred acids are formic acid, acetic acid, propionic acid and butyric acid. It has been found that formic acid is especially suitable as formic acid was observed to give only limited decomposition of the organic hydroperoxide.

The concentration of acid in the aqueous solution preferably is from 0.0001 to 5 %wt, based on total amount of aqueous solution, more preferably from 0.001 to 2 %wt, most preferably from 0.001 to 1 %wt.

Preferably, the water for use in steps (c) and/or (d) consists of waste water optionally in combination with clean water and has a pH of from 2 to 7, preferably

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of from 3 to less than 7, more preferably of from 3.5 to 6.5.

Waste water streams can be used as such. However, in some cases it might be advantageous to concentrate the waste water stream before use in the process according to the present invention.

Dependent on the amount of contaminants present in the hydrocarbonaceous phase containing organic peroxide, the washing with water is either carried out once or a number of times. Preferably, the washing is carried out of from 1 to 3 times.

In optional process step (e), at least part of the hydrocarbonaceous phase containing organic hydroperoxide obtained in steps (c) and/or (d) is contacted with olefin, preferably propene, in the presence of a catalyst to obtain alkylaryl hydroxide and oxirane compounds. A catalyst which can suitably be used in such process comprises titanium on silica and/or silicate. A preferred catalyst is described in EP-A-345856. The reaction generally proceeds at moderate temperatures and pressures, in particular at temperatures in the range of from 0 to 200 °C, preferably in the range from 25 to 200 °C. The precise pressure is not critical as long as it suffices to maintain the reaction mixture as a liquid or as a mixture of vapour and liquid. Atmospheric pressure may be satisfactory. In general, pressures can be in the range of from 1 to 100 x 10⁵ N/m².

The oxirane compounds can be separated from the reaction product containing alkylaryl hydroxide in any way known to be suitable to someone skilled in the art. The liquid reaction product may be worked up by fractional distillation, selective extraction and/or filtration. The solvent, the catalyst and any unreacted olefin or alkylaryl hydroperoxide may be recycled for further utilization.

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The alkylaryl hydroxide obtained in the process can be dehydrated in the presence of a catalyst to obtain styrene and water. Process which can be used for this step have been described in WO 99/42425 and WO 99/42426. However, any suitable process known to someone skilled in the art can in principle be used.

The present invention is further illustrated by the following examples.

Comparative Example 1

In a reactor, air was blown through ethylbenzene. The product obtained contained ethylbenzene hydroperoxide. This product was contacted with a solution containing 0.5 %wt NaOH in water and mixed at a temperature of 60 °C. The weight ratio of product containing ethylbenzene hydroperoxide to NaOH containing solution was 4.5:1 (wt:wt). The neutralized mixture obtained was sent to a settling vessel where a neutralized hydrocarbonaceous phase containing ethylbenzene hydroperoxide was separated from an aqueous phase.

The neutralized hydrocarbonaceous phase containing ethylbenzene hydroperoxide was sent to a coalescer where further aqueous phase was removed. The neutralized hydrocarbonaceous phase containing ethylbenzene hydroperoxide, was washed by mixing the neutralized ethylbenzene hydroperoxide solution from the coalescer with an aqueous solution, separating the mixture obtained in a settling vessel into an aqueous phase and a hydrocarbonaceous phase, subsequently separating the hydrocarbonaceous phase obtained from the settling vessel with the help of a first coalescer, and separating the hydrocarbonaceous phase obtained in the first coalescer with the help of a second coalescer. Each of these steps is described in more detail herein below. The hydrocarbonaceous phase obtained in the second coalescer

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contains ethylbenzene hydroperoxide, ethyl benzene, water and contaminants. This hydrocarbonaceous phase is distilled. The distillate contains ethyl benzene, water and contaminants. This distillate was phase separated in a vessel to obtain a hydrocarbonaceous phase containing ethyl benzene and contaminants, and an aqueous phase containing water and contaminants. The latter had a pH of 3 and was used as wastewater for use in the aqueous solution for washing the neutralized hydrocarbonaceous phase.

The neutralized ethylbenzene hydroperoxide solution was mixed with an aqueous solution in a ratio of 4.5:1 (wt:wt). The aqueous solution comprised 85 %wt of water which is being recycled in this process step to which is added 1.3 %wt of clean water and 13.7 %wt of wastewater which had been used in washing a hydrocarbonaceous phase containing organic hydroperoxide.

The mixture which was obtained, was sent to a settling vessel where a hydrocarbonaceous phase was separated from an aqueous phase.

NaOH was added to the aqueous phase obtained, which NaOH containing aqueous phase was for use in the neutralization of the hydrocarbonaceous phase containing ethylbenzene hydroperoxide.

The hydrocarbonaceous phase obtained in the settler, was sent to a first coalescer where were added 1.1 %wt (based on total hydrocarbonaceous phase) of the distillate aqueous phase containing water and contaminants described above, and 1.7 %wt (based on total hydrocarbonaceous phase) of clean water. An aqueous phase and a hydrocarbonaceous phase were obtained in the first coalescer. The hydrocarbonaceous phase from the first coalescer was sent to the second coalescer where further 1.4 %wt (based on total hydrocarbonaceous phase) of clean water were added.

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It was found that the hydrocarbonaceous phase obtained from the second coalescer, contained about 1 ppm of sodium.

Example 1

5 Comparative Example 1 was repeated except that the NaOH containing aqueous phase which was recycled to the neutralization step was filtered with the help of a Whatman polypropylene filter having openings of at most 0.4 micrometers before being used again in the
10 neutralization step.

It was found that the hydrocarbonaceous phase obtained from the second coalescer, contained substantially less than 1 ppm of sodium. Additionally, it was found that the pressure over the filter gradually
15 increased from $0.05 \times 10^5 \text{ N/m}^2$ to $1 \times 10^5 \text{ N/m}^2$ in the course of 3 weeks. This indicates that solids are being separated off.

Example 2

20 Waste water was obtained in the dehydration of 1-phenyl ethanol to styrene. The waste water obtained was distilled whereby the distillate obtained contains water and organic compounds. Organic phase was separated off from the distillate in a settler. The aqueous phase was sent from the settler to a coalescer. The aqueous phase
25 obtained in the coalescer contained 10 ppm of solids of which 2 ppm was iron. To this aqueous phase was added 20 %wt of NaOH. Thus obtained NaOH solution was filtered with the help of a polypropylene filter having openings of different maximum sizes. The filtrate was contacted
30 with a solution of ethylbenzene hydroperoxide in ethylbenzene at 70 °C for several hours. In a comparative example, the NaOH solution had not been filtered before use. The following results were obtained.

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filter size (micrometre)	none	40	20	10	6
rag formation	strong	slight	none	none	none

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C L A I M S

1. Process for preparing organic hydroperoxides, which process comprises:

(a) oxidation of an organic compound to obtain reaction product containing organic hydroperoxide,

5 (b) treating at least part of the organic hydroperoxide containing reaction product with a basic aqueous solution and separating hydrocarbonaceous phase containing organic hydroperoxide from basic aqueous phase,

10 (c) washing with water at least part of the separated hydrocarbonaceous phase containing organic hydroperoxide and separating hydrocarbonaceous phase containing organic hydroperoxide from aqueous phase, and

(d) optionally repeating step (c) one or more times, in which process solid particles are removed from the reaction product containing organic hydroperoxide and/or basic aqueous solution before use in step (b).

2. Process according to claim 1, in which process solid particles are removed by filtering at least part of the reaction product containing organic hydroperoxide and/or at least part of basic aqueous solution before use in step (b).

3. Process for preparing oxirane compounds, which process comprises preparing an alkylaryl hydroperoxide with the help of the process according to claim 1 or 2 in which the organic compound is an alkylaryl compound, and which process further comprises:

25 (e) contacting at least part of the hydrocarbonaceous phase containing alkylaryl hydroperoxide obtained in step (c) and/or (d) with olefin and catalyst to obtain alkylaryl hydroxide and oxirane compounds, and

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(f) separating at least part of the oxirane compound from the alkylaryl hydroxide.

4. Process for preparing an alkenyl aryl compound, which process comprises preparing an alkylaryl hydroxide with the help of the process according to claim 3, which process further comprises:

(g) converting at least part of the alkylaryl hydroxide obtained in step (f).

5. Process according to any one of claims 2 to 4, in which process the filtering is carried out with the help of a filter having openings of 50 micrometres or less.

6. Process according to any one of claims 2 to 5, in which process at least part of the basic aqueous solution which has been separated off in step (b) is filtered and subsequently recycled to step (b).

7. Process according to any one of claims 1 to 6, in which process the basic aqueous solution contains fresh basic aqueous solution, recycled basic aqueous solution and optionally additional water.

8. Process according to any one of claims 1 to 7, in which process step (c) and/or (d) at least part of the separated hydrocarbonaceous phase containing organic hydroperoxide is washed with waste water optionally in combination with clean water.