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Continuous process for manufacturing oxirane, comprising purification steps

The present invention relates to a process for manufacturing oxirane by reaction between an olefin and a peroxide compound in the presence of a catalyst and a solvent. In particular, the invention relates to the manufacture of propylene oxide by epoxidation of propylene using hydrogen peroxide in the presence of a catalyst containing TS-1.

It is known practice to manufacture propylene oxide by reaction between propylene and a peroxide compound in the presence of TS-1. For example, in patent US-A-5 849 937, such a process is performed in several reactors arranged in series. In this continuous process, the medium leaving the last reactor may be fractionated or treated in another manner to recover the epoxide. The unconverted olefin may be recycled.

However, in this process, the medium leaving the last reactor contains, besides the unconverted olefin, the solvent and optionally water. This present process has the drawback in that it is relatively uneconomical since it is not envisaged to recover the solvent.

The present invention is directed towards overcoming this drawback by providing a novel process which makes it possible to recover the solvent simply, to remove the water and to minimize the consumption of steam and/or power.

To this end, the invention relates to a continuous process for manufacturing oxirane by reacting an olefin with a peroxide compound in the presence of a catalyst, a solvent and water in a plant comprising at least one reactor containing the catalyst and at least two distillation columns, according to which:

- the olefin, the solvent, the peroxide compound and the water are introduced into the reactor,
- an epoxidation of the olefin is carried out to form the oxirane,

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- a medium comprising the oxirane formed, the unconverted olefin, the solvent, the unconsumed peroxide compound, the water and possibly by-products is removed from the reactor,
- the medium is introduced into a distillation column (A),
- a mixture containing the majority of the oxirane formed and unconverted olefin, solvent, water and possibly by-products is collected at the top of column (A),
- the mixture is introduced into a condenser to eliminate some of the unconverted olefin,
- the mixture depleted in unconverted olefin is collected in liquid form,
- the liquid mixture is introduced into a second distillation column (B),
- a mixture of solvent and water is collected at the bottom of column (B) and is recycled into the reactor, and
- an oxirane-based medium is collected at the top of column (B).

One of the essential characteristics of the present invention lies in the possibility of directly recycling, into the reactor without any purification and/or water-removal treatment, the medium collected at the bottom of column (B). This makes it possible to recover the solvent in a simple manner without a purification treatment, while at the same time maintaining good production efficiency.

The distillation in column (A) serves to remove as quickly as possible the oxirane as soon as it is formed in the reaction medium, in order to prevent it from coming into contact with the other constituents of the reaction medium and in order to prevent by-products from being thus formed. Specifically, the Applicant has found that when propylene oxide is manufactured using an aqueous hydrogen peroxide solution as peroxide compound and methanol as solvent, by-products are formed by reaction between propylene oxide and water or

methanol, and in particular propylene glycol and methoxypropanols of formula CH_3-CHOH-CH_2-OCH_3 and CH_3-CH(OCH_3)-CH_2OH. When epichlorohydrin is manufactured, by-products are formed by reaction between epichlorohydrin and water or methanol, and in particular 1-chloropropanediol and chloromethoxy-propanols of formulae $ClCH_2$-CHOH-CH_2-OCH_3 and Cl-CH_2-CH(OCH_3)-CH_2OH. The formation of by-products reduces the selectivity of the process and consequently its yield.

The separation in column (A) is carried out in a distillation column which is separate and distinct from the epoxidation reactor. Since the catalyst does not leave the epoxidation reactor, the distillation is thus carried out in the absence of the epoxidation catalyst, in order to avoid contact between the oxirane formed and the epoxidation catalyst, since this catalyst would promote the formation of by-products.

The mixture collected at the top of column (A) generally contains:

- oxirane in a concentration of from 30% to 90% by weight, usually from 45% to 75% by weight;
- unconverted olefin in a concentration of from 2% to 20% by weight, usually from 5% to 15% by weight;
- solvent in a concentration of from 5% to 40% by weight, usually from 10% to 25% by weight;
- water in a concentration of less than 5% by weight, usually less than 2% by weight;

The mixture collected at the bottom of column (A) generally contains:

- solvent in a concentration of from 25% to 99% by weight, in particular from 50% to 95% by weight;
- unconverted olefin in a concentration of less than 1% by weight, in particular less than 0.1% by weight;

- unconsumed peroxide compound in a concentration of from 0.1% to 10% by weight, in particular from 0.2% to 6% by weight;
- water in a concentration of from 5% to 60% by weight, in particular from 20% to 50% by weight;
- by-products in a concentration of from 0.1% to 10% by weight, in particular from 0.2% to 6% by weight.

The condenser located downstream of column (A) serves to remove some of the unconverted olefin present in the medium entering the condenser, and to recover a mixture depleted in unconverted olefin in liquid form. The liquid mixture leaving the condenser generally contains not more than 2% by weight of unconverted olefin, in particular not more than 0.5% by weight.

The distillation in column (B) serves to separate the solvent and the water from the medium entering column (B). After separation, the medium containing the oxirane, which is collected at the top of column (B), generally contains not more than 10% by weight of solvent, in particular not more than 5% by weight. It usually contains not more than 0.5% by weight of water, in particular not more than 0.1% by weight.

The mixture of solvent and water collected at the bottom of column (B) generally contains:

- from 25% to 99% by weight of solvent, in particular from 50% to 95% by weight; and
- from 0 to 20% by weight of water, in particular from 0% to 10% by weight.

The conditions under which each distillation (in columns (A) and (B)) is carried out depend on the nature of the oxirane (and in particular on its boiling point), its concentration in the medium introduced into the distillation column, the nature of the other constituents of the medium, their boiling point and the desired distillation yield.

Each distillation is generally carried out at a temperature of greater than or equal to 10°C, preferably greater than or equal to 40°C, values of greater than or equal to 50°C being recommended. The temperature is usually less than or equal to 125°C, most typically less than or equal to 110°C, values of less than or equal to 100°C being preferred.

Each distillation is commonly carried out at a temperature of greater than or equal to 0.2 bar, preferably greater than or equal to 0.5 bar, values of greater than or equal to 1 bar being the most common. The pressure is generally less than or equal to 5 bar, in particular less than or equal to 3 bar, values of less than or equal to 2 bar being most particularly recommended. In the present description, all reference to the distillation pressure corresponds to the absolute pressure measured at the top of the distillation column.

Each distillation column which may be used in the process according to the invention is known per se. It is possible to use, for example, a column with conventional plates or a column with plates of "dual-flow" type or alternatively a column with loose or structured packing.

Each distillation makes it possible to separate the majority of the oxirane formed from the epoxidation reaction medium. This majority is generally greater than or equal to 80% of the amount of oxirane formed in the first reactor. It is usually greater than or equal to 90%. Usually, it is less than or equal to 99.9%. In particular, it is less than or equal to 99%.

The number of theoretical plates in each distillation column is generally greater than or equal to 20, more especially greater than or equal to 40. A number of less than or equal to 80 gives good results. A number of less than or equal to 60 is recommended.

The degree of molar reflux (which corresponds to the molar flow rate of liquid sent to the top of the column relative to the distillate as a whole - vapour

plus liquid - taken at the top of the column) in each distillation column is usually greater than or equal to 0.5, preferably greater than or equal to 0.8. This degree is commonly less than or equal to 5, usually less than or equal to 2.5.

In a first particular embodiment of the process according to the invention, the medium collected at the top of column (B) is introduced into a third distillation column (C) and unconverted olefin is collected at the top of column (C). This olefin may be advantageously recycled into the reactor.

The distillation in column (C) serves to remove the unconverted olefin from the medium entering column (C) and thus to free the medium containing the oxirane from unconverted olefin. When the olefin introduced into the reactor contains impurities, in general light impurities, these are also removed in column (C). Mention may be made, by way of example, of propylene sources which contain up to 10% by weight of propane.

The distillation in column (C) may be carried out under the conditions specified above for columns (A) and (B).

The medium collected at the top of column (C) generally contains:

- from 30% to 90% by weight of olefin, in particular from 40% to 70% by weight; and
- from 10% to 70% by weight of impurities introduced with the olefin into the reactor, in particular from 30% to 60% by weight.

The medium collected at the bottom of column (C) generally contains not more than 0.05% by weight of unconverted olefin, in particular not more than 0.01% by weight. It generally contains not more than 0.1% by weight of impurities introduced with the olefin, in particular not more than 0.02% by weight.

In a second embodiment of the process according to the invention, the medium collected from the bottom of column (C) is introduced into a fourth distillation column (D) and the oxirane formed is collected at the

top of column (D). The reaction medium at the bottom of column (D), which contains by-products, may advantageously be recycled into column (B). This recycling makes it possible to remove from the oxirane the by-products formed in column (C) by reaction of the oxirane with the solvent (in particular the alcohol) and water or by corrosion while at the same time allowing the oxirane entrained to be recovered.

The distillation in column (D) serves to remove the heavy impurities such as the by-products described above from the medium entering column (D), the by-products formed in column (D) itself and the corrosion products, and thus to free the medium containing the oxirane from heavy impurities.

The distillation in column (D) can be carried out under the conditions specified above for columns (A) and (B).

The final product collected at the top of column (D) generally contains not more than 0.1% by weight of heavy impurities, in particular not more than 0.01% by weight. It generally contains at least 95% by weight of oxirane, in particular at least 98%, preferably at least 99.5% by weight. A purity of 99.9% or even 99.99% by weight may be expected.

In a third embodiment of the process according to the invention, the reactor consists of two reactors arranged in parallel, the two reactors possibly being operated simultaneously or alternately. This third embodiment has the advantage of being able to manufacture the oxirane continuously in a relatively constant yield although the catalytic activity of the epoxidation catalyst falls over time. Specifically, this embodiment makes it possible to stop one of the two reactors in order to regenerate or replace the catalyst present therein while the other reactor continues to operate.

In a fourth embodiment of the process according to the invention, the medium removed from the reactor is first subjected to a depressurization before being

introduced into column (A). This embodiment is particularly suitable when the epoxidation is carried out under pressure or in the presence of a gaseous compound. This gaseous compound may be the olefin itself (for example propylene) or an inert gas which is introduced into the epoxidation reaction medium to allow the oxirane to be entrained and removed from the reactor, as disclosed in patent application WO 99/48883 by the Applicant.

In a fifth embodiment of the process according to the invention, the catalyst is present in the reactor in the form of particles, at least some of which is in fluidized form, as disclosed in the Applicant's patent application filed on the same day as the present patent application and entitled "Process for manufacturing oxirane in the presence of a catalyst in the form of particles" (the content of which is incorporated by reference). This embodiment makes it possible to obtain a homogeneous dispersion of the catalyst in the epoxidation reaction medium, good heat exchange and thus easy control of the reaction temperature. In this embodiment, it is recommended that the medium leaving the reactor should pass through a filter before being introduced into column (A) or, where appropriate, before being subjected to the depressurization.

In a sixth preferred embodiment, the plant comprises at least two reactors arranged in series, each of which contains some of the catalyst, and at least three distillation columns, and according to which:

- a first portion of the olefin, the solvent and the peroxide compound are introduced into a first reactor,
- an epoxidation of the first portion of the olefin is carried out therein to form a first portion of the oxirane,
- a medium comprising the first portion of oxirane formed, the solvent, the unconverted

olefin, the unconsumed peroxide compound and possibly by-products is removed from this first reactor,

- the medium is introduced into a first distillation column (A),
- a first mixture containing the majority of the oxirane formed and unconverted olefin, solvent, water and possibly by-products is collected at the top of column (A),
- a first medium depleted in oxirane, containing solvent, unconverted olefin, unconsumed peroxide compound and possibly by-products, is collected at the bottom of column (A),
- the first medium depleted in oxirane, a second portion of the olefin and optionally a second portion of the peroxide compound are introduced into a second reactor,
- an epoxidation of the second portion of the olefin is carried out therein in order to form a second portion of the oxirane,
- a medium comprising the second portion of oxirane formed, solvent, unconverted olefin, unconsumed peroxide compound and possibly by-products is removed from this second reactor,
- the medium is introduced into another distillation column (A'),
- a second mixture containing the majority of the oxirane formed and unconverted olefin, solvent, water and possibly by-products is collected at the top of column (A'),
- a second medium depleted in oxirane, containing solvent, unconverted olefin, unconsumed peroxide compound and possibly by-products, is collected at the bottom of column (A'),
- each of the first and second mixtures containing the majority of the oxirane formed and the unconverted olefin is introduced into a condenser to separate out some of the unconverted olefin,

- a mixture depleted in unconverted olefin is removed in liquid form from each condenser,
- the liquid mixture is introduced into a second distillation column (B),
- a mixture of solvent and water is collected at the bottom of column (B) and is recycled into the first reactor, and
- an oxirane-based medium is collected at the top of column (B).

In this sixth embodiment of the process according to the invention, it may be advantageous to introduce all of the peroxide compound into the first reactor, as disclosed in the Applicant's patent application filed on the same day as the present patent application and entitled "Process for manufacturing oxirane using a peroxide compound" (the content of which is incorporated by reference). The subsequent reactor(s) is (are) thus not fed with fresh peroxide compound, but only with the peroxide compound which is present in the medium from the previous reactor and which was not consumed in this previous reactor. The fact that no peroxide compound is added to the subsequent reactor(s) makes it possible to consume 100% of the total amount of peroxide compound used without, however, reducing the reaction rate compared with a process using the same total amount of peroxide compound but in which each reactor is fed with fresh peroxide compound.

In this sixth embodiment of the process according to the invention, it may be advantageous to recycle a fraction of the medium produced at the bottom of one of columns (A) and (A') into the reactor directly upstream. This makes it possible to keep the circulation rate of the reaction medium in the reactor constant and not to disrupt the flow. This practice is particularly advantageous when the catalyst is used in fluidized form.

In this sixth embodiment, the plant may obviously comprise more than two reactors connected in

series. The plant preferably comprises three reactors arranged in series. In this case:

- a third portion of the olefin, the second medium collected at the bottom of column (A') and optionally a third portion of the peroxide compound are introduced into a third reactor,
- an epoxidation of the third portion of olefin is carried out therein in order to form a third portion of the oxirane,
- a medium comprising the third portion of oxirane, the solvent, the unconverted olefin, possibly the unconsumed peroxide compound and possibly by-products is removed from this third reactor,
- this medium is introduced into yet another distillation column (A"),
- a medium is collected at the top of column (A") and is recycled, after condensation, into the first reactor,
- an a aqueous effluent is collected at the bottom of column (A").

The distillations in columns (A') and (A") have the same function as that in column (A) and may be carried out as in column (A).

In this sixth embodiment, each reactor is fed with olefin. The peroxide compound and the solvent are introduced into the first reactor. Fresh peroxide compound may also be introduced into one or more of the subsequent reactors. Each reactor contains some of the catalyst which does not leave this reactor. When the catalyst is present in the form of a fixed bed, it is generally not necessary to take precautions to keep the catalyst in the reactor. On the contrary, when the catalyst is present in the form of particles at least some of which are in fluidized form, it is recommended to include a fall-out zone above the fluid bed to stop the particles of catalyst which are in motion and/or to include a filter at the reactor outlet.

In this sixth embodiment, reactors of identical size are preferably used. This makes it possible to interchange the functioning of the reactors when the deactivated catalyst of a reactor is replaced with fresh or regenerated catalyst without interfering with the functioning of the plant (so-called "carousel" functioning).

The embodiments described above may be combined together.

One embodiment which is suitable is represented diagrammatically in Figure 1. In this embodiment, the reactor 1 contains the catalyst, preferably in a fluid bed 2. The reactor 1 is fed with olefin via pipe 3 and then via pipe 4, with peroxide compound via pipe 5 and then via pipe 4, and with solvent via pipe 4 from another part of the plant which is described later. In the reactor, the olefin reacts with the peroxide compound in the presence of the catalyst to form the oxirane. The medium leaving the reactor 1 via pipe 6 contains the solvent, the oxirane, the unconsumed peroxide compound, the unconverted olefin and possibly by-products. This medium passes through a filter 7 and is conveyed via pipe 8 into the container 9 in which it undergoes a depressurization. The medium is then transported via pipe 10 into a distillation column (A). A medium containing solvent, unconsumed peroxide compound and possibly by-products is collected at the bottom of the distillation column (A). This medium, some of which may be recycled into the reactor via pipes 11 and 4, is purged to remove an aqueous effluent which contains the impurities. A mixture of oxirane and unconverted olefin is recovered at the top of column (A). This mixture is conveyed via pipe 12 into a condenser 13 which separates the oxirane from the unconverted olefin. The unconverted olefin is recycled into the reactor 1 via pipes 14, 3 and 4. A purge 21 makes it possible to remove the gaseous impurities. The liquid mixture depleted in olefin and collected from the condenser is conveyed via pipe 15 into a

distillation column (B). The mixture of solvent and water collected in the bottom of column (B) is recycled via pipe 4 into the reactor 1. The medium collected at the top of column (B), which contains the oxirane and which is freed of solvent and water, is conveyed via pipe 16 into a distillation column (C). The unconverted olefin is collected at the top of column (C) and recycled via pipes 17, 14, 3 and 4 into the reactor 1. The medium collected at the bottom of column (C), which contains the oxirane and which is freed of solvent, water and unconverted olefin, is conveyed via pipe 18 into a distillation column (D). The heavy impurities are collected at the bottom of column (D) and recycled via pipe 19 into column (B). The oxirane freed of solvent, water, unreacted olefin and light and heavy impurities is collected, via pipe 20, at the top of column (D).

One embodiment which is particularly preferred is represented diagrammatically in Figure 2. Three reactors arranged in series are used therein. In this embodiment, the reactors 1, 2 and 3 each contain a portion of the catalyst, preferably as a fluid bed 4, 5 and 6. The reactor 1 is fed with a first portion of the olefin via pipe 7 and then via pipe 8, with peroxide compound via pipe 9 and then via pipe 8, and with solvent via pipe 8 from another part of the plant which is described later. In the reactor 1, the first portion of the olefin reacts with the peroxide compound in the presence of the catalyst to form a first portion of the oxirane. The medium leaving reactor 1 via pipe 10 contains the solvent, the first portion of the oxirane, the unconsumed peroxide compound, the unconverted olefin and possibly by-products. This medium passes through a filter 11 and is conveyed via pipe 12 into the container 13 in which it undergoes a de-pressurization. The medium is then transported via pipe 14 into a distillation column (A). A medium containing solvent, unconsumed peroxide compound and possibly some of the unconverted olefin is collected at

the bottom of the distillation column (A). This medium is transported via pipe 15 into the second reactor 2. The reactor 2 is fed with a second portion of the olefin via pipe 16. In the reactor 2, the second portion of the olefin reacts with the unconsumed peroxide compound from the first reactor in the presence of catalyst 5 to form a second portion of the oxirane. The medium leaving the reactor 2 via pipe 17 thus contains solvent, the second portion of the oxirane, unconverted olefin and peroxide compound not consumed in reactor 2. This medium passes through a filter 18 and is conveyed via pipe 19 into the container 20 in which it undergoes a depressurization. The medium is then transported via pipe 21 into a distillation column (A'). Two mixtures of oxirane and of unconverted olefin are recovered at the top of each column (A) and (A'). These mixtures are respectively conveyed via pipes 22 and 23 into condensers 24 and 25 which separate the oxirane from the unconverted olefin. The unconverted olefin is recycled into the reactor 1 via pipes 26, 7 and 8, for the olefin from column (A), and via pipes 27, 26, 7 and 8 for the olefin from column (A'). A purge 43 makes it possible to evacuate the gaseous impurities. The liquid mixtures depleted in olefin and collected from the condensers are conveyed via pipes 28 and 29 into a distillation column (B). The mixture of solvent and water collected at the bottom of column (B) is recycled via pipes 30, 7 and 8 into the reactor 1. The medium collected at the top of column (B), which contains the oxirane and which is freed of solvent and water, is conveyed via pipe 31 into a distillation column (C). The unconverted olefin is collected at the top of column (C) and recycled via pipes 32, 26, 7 and 8 into the reactor 1. The medium collected at the bottom of column (C), which contains the oxirane and which is freed of solvent, water and unconverted olefin, is conveyed via pipe 33 into a distillation column (D). The heavy impurities are collected at the bottom of column (D) and recycled via

pipe 34 into column (B). The oxirane freed of solvent, water, unconverted olefin and light and heavy impurities is collected, via pipe 44, at the top of column (D). A medium containing solvent, peroxide compound not consumed in the reactor 2 and possibly some of the unconverted olefin is collected at the bottom of column (A'). This medium is transported via pipe 35 into the third reactor 3. The reactor 3 is fed with a third portion of the olefin via pipe 36. In the reactor 3, the third portion of the olefin reacts with the unconsumed peroxide compound from the second reactor in the presence of catalyst 6 to form a third portion of the oxirane. The conditions in the reactor 3 are such that all of the peroxide compound not yet consumed in the second reactor is consumed in the reactor 3. The medium leaving the reactor 3 via pipe 37 thus contains solvent, the third portion of the oxirane, unconverted olefin and possibly by-products. This medium passes through a filter 38 and is conveyed via pipe 39 into a distillation column (A"). An aqueous effluent is collected, via pipe 40, at the bottom of column (A"). The medium collected at the top of column (A") is conveyed via pipe 41 into a condenser 42 and is then recycled via pipe 8 into the first reactor 1.

The catalyst used in the process according to the invention generally contains a zeolite as active element, and preferably a titanium zeolite. The term "titanium zeolite" is intended to denote a solid containing silica which has a microporous crystal structure of zeolite type and in which several silicon atoms are replaced with titanium atoms. The titanium zeolite advantageously has a crystal structure of ZSM-5, ZSM-11, ZSM-12, MCM-41 or ZSM-48 type. It may also have a crystal structure of beta zeolite type, preferably free of aluminium. Zeolites with an infrared absorption band at about 950-960 cm^{-1} are suitable for use. Titanium zeolites of silicalite type are preferred. Those corresponding to the formula $xTiO_2(1-x)SiO_2$ in which x is from 0.0001 to 0.05 and

preferably from 0.001 to 0.05 give high performance. Materials of this type, known under the name TS-1, have a microporous crystalline zeolite structure similar to that of zeolite ZSM-5.

The catalyst used in the process according to the invention is advantageously in the form of particles obtained by extrusion as disclosed in the Applicant's patent application WO 99/28029, or by a spray process as disclosed in the Applicant's patent application WO 99/24164. The content of these two patent applications is incorporated herein by reference.

The solvent used in the process according to the invention may be chosen from saturated, linear or branched aliphatic alcohols. The alcoholic solvent generally contains up to 10 carbon atoms, preferably from 1 to 6 carbon atoms. Examples which may be mentioned are methanol and ethanol. Methanol is preferred.

The amount of solvent used in the first reactor is generally at least 25% by weight of the liquid reaction medium present in the first reactor, in particular at least 40% by weight, for example at least 50% by weight. This amount usually does not exceed 99% by weight and in particular does not exceed 95% by weight.

The molar ratio between the amounts of olefin and of peroxide compound used in the process according to the invention is generally at least 0.1, in particular at least 0.2 and preferably at least 0.5. This molar ratio is usually not more than 100, in particular not more than 50 and preferably not more than 25.

In the process according to the invention, the peroxide compound is generally used in the first reactor in an amount of at least 0.005 mol per hour and per gram of catalyst present in the first reactor, in particular of at least 0.01 mol. The amount of peroxide compound is usually less than or equal to 25 mol and in

particular less than or equal to 10 mol. Preference is shown for an amount of peroxide compound of greater than or equal to 0.03 mol and less than or equal to 2.5 mol.

In the process according to the invention, the peroxide compound is advantageously used in the form of an aqueous solution. In general, the aqueous solution contains at least 2% by weight of peroxide compound, in particular at least 5% by weight. It usually contains not more than 90% by weight of peroxide compound, in particular 70% by weight. A concentration of 30% to 40% by weight, for example about 36% by weight, is particularly suitable.

The reaction temperature between the olefin and the peroxide compound may range from 10°C to 125°C. In one advantageous variant as disclosed in patent application EP 99/08703 by the Applicant, it is greater than 35°C to overcome the gradual deactivation of the catalyst. The temperature may be greater than or equal to 40°C and preferably greater than or equal to 45°C. A temperature of greater than or equal to 50°C is more particularly preferred. The reaction temperature is preferably less than 100°C.

In the process according to the invention, the reaction between the olefin and the peroxide compound may take place at atmospheric pressure. It may also be performed under pressure. This pressure generally does not exceed 40 bar. A pressure of 20 bar is suitable in practice.

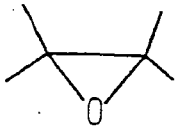
The peroxide compounds which may be used in the process according to the invention are peroxide compounds containing one or more peroxide functions (-OOH) which may release active oxygen and which are capable of carrying out an epoxidation. Hydrogen peroxide and peroxide compounds which may produce hydrogen peroxide under the conditions of the epoxidation reaction are suitable for use. Hydrogen peroxide is preferred.

When hydrogen peroxide is used, it may be advantageous to use, in the process according to the invention, an aqueous hydrogen peroxide solution in crude form, i.e. in unpurified form. For example, a solution obtained by simple extraction with substantially pure water of the mixture derived from the oxidation of at least one alkylanthrahydroquinone (process known as "autoxidation AO process") without a subsequent washing and/or purification treatment may be used. These crude hydrogen peroxide solutions generally contain from 0.001 to 10 g/l of organic impurities expressed as TOC (Total Organic Carbon). They usually contain metal cations (such as alkali metals or alkaline-earth metals, for instance sodium) and anions (such as phosphates and nitrates) in contents of from 0.01 to 10 g/l.

In another variant of the process, a hydrogen peroxide solution produced by direct synthesis using oxygen and hydrogen in the presence of methanol may be used.

When hydrogen peroxide is used, a small amount of decomposition thereof into water and oxygen may be encountered during the process. This oxygen is found in the unconverted olefin. In order to prevent any risk of explosion, it is recommended to treat the gas shuttle containing the unconverted olefin and the oxygen in order to remove the oxygen. This treatment may be carried out, for example, by using a pervaporation operation by means of membranes or alternatively by a chemical treatment, for example with sulphite.

The oxirane which may be prepared by the process according to the invention is an organic compound comprising a group corresponding to the general formula:



The oxirane generally contains from 2 to 10 carbon atoms, preferably from 3 to 6 carbon atoms. The

oxiranes which may be prepared advantageously by the process according to the invention are 1,2-epoxypropane and 1,2,-epoxy-3-chloropropane. The preferred oxirane is 1,2-epoxypropane.

The olefins which are suitable in the process according to the invention generally contain from 2 to 10 carbon atoms and preferably 3 to 6 carbon atoms. Propylene, butylene and allyl chloride are suitable for use. Propylene and allyl chloride are preferred, and most particularly propylene.

In the process according to the invention, it may prove to be advantageous to monitor the pH of the liquid phase. For example, it may be advantageous to maintain the pH of the liquid phase during the reaction between the olefin and the peroxide compound at a value of from 4.8 to 6.5, for example by adding a base (sodium hydroxide) to the epoxidation medium, as recommended in patent application WO 99/48882 by the Applicant (the content of which is incorporated by reference into the present patent application). This base may be introduced into a single reactor (for example the first reactor) or into several reactors. It is preferably introduced into each reactor.

The reaction between the olefin and the peroxide compound may be carried out in the presence of a salt such as sodium chloride, as disclosed in patent application WO EP 99/08703 by the Applicant (the content of which is incorporated by reference into the present patent application). This salt may be introduced into a single reactor (for example the first reactor) or into several reactors. It is preferably introduced into each reactor.

It may be advantageous to introduce the olefin in a form diluted in one or more alkanes. For example, a fluid containing the olefin and also at least 10% (in particular 20%, for example at least 30%) by volume of one or more alkanes may be introduced into the epoxidation reactors. For example, in the case of propylene, the latter may be mixed with at least 10% by

volume of propane when the recycled unconverted propylene is introduced into the reactor. It may also be a source of propylene which is not completely freed of propane.

The process according to the invention gives the best results when the oxirane is propylene oxide, the olefin is propylene, the peroxide compound is hydrogen peroxide, the solvent is methanol and the catalyst contains TS-1.

CLAIMS

1. Continuous process for manufacturing oxirane by reacting an olefin with a peroxide compound in the presence of a catalyst, a solvent and water in a plant comprising at least one reactor containing the catalyst and at least two distillation columns, according to which:

- the olefin, the solvent, the peroxide compound and the water are introduced into the reactor,
- an epoxidation of the olefin is carried out to form the oxirane,
- a medium comprising the oxirane formed, the unconverted olefin, the solvent, the unconsumed peroxide compound, the water and possibly by-products is removed from the reactor,
- the medium is introduced into a distillation column (A),
- a mixture containing the majority of the oxirane formed and unconverted olefin, solvent, water and possibly by-products is collected at the top of column (A),
- the mixture is introduced into a condenser to eliminate some of the unconverted olefin,
- the mixture depleted in unconverted olefin is collected in liquid form,
- the liquid mixture is introduced into a second distillation column (B),
- a mixture of solvent and water is collected at the bottom of column (B) and is recycled into the reactor, and
- an oxirane-based medium is collected at the top of column (B).

2. Process according to Claim 1, in which the medium collected at the top of column (B) is introduced into a third distillation column (C), unconverted olefin is collected at the top of column (C) and is recycled into the reactor.

3. Process according to Claim 2, in which the medium collected at the bottom of column (C) is

introduced into a fourth distillation column (D), the oxirane formed is collected at the top of column (D) and a medium containing by-products is collected at the bottom of column (D) and recycled into column (B).

4. Process according to any one of Claims 1 to 3, in which the reactor consists of two reactors arranged in parallel, the two reactors possibly being operated simultaneously or alternately.

5. Process according to any one of Claims 1 to 4, in which the medium removed from the reactor is first subjected to a depressurization before being introduced into column (A).

6. Process according to any one of Claims 1 to 5, in which the catalyst is present in the reactor in the form of particles, at least some of which are in fluidized form.

7. Process according to Claim 6, in which the medium leaving the reactor passes through a filter before being introduced into column (A) or, where appropriate, before being subjected to depressurization.

8. Process according to any one of Claims 1 to 7, in which the plant comprises at least two reactor arranged in series, each of which contains some of the catalyst, and at least three distillation columns, and according to which:

- a first portion of the olefin, the solvent and the peroxide compound are introduced into a first reactor,
- an epoxidation of the first portion of the olefin is carried out therein to form a first portion of the oxirane,
- a medium comprising the first portion of oxirane formed, the solvent, the unconverted olefin, the unconsumed peroxide compound and possibly by-products is removed from this first reactor,
- the medium is introduced into a first distillation column (A),

- a first mixture containing the majority of the oxirane formed and unconverted olefin, solvent, water and possibly by-products is collected at the top of column (A),
- a first medium depleted in oxirane, containing solvent, unconverted olefin, unconsumed peroxide compound and possibly by-products, is collected at the bottom of column (A),
- the first medium depleted in oxirane, a second portion of the olefin and optionally a second portion of the peroxide compound are introduced into a second reactor,
- an epoxidation of the second portion of the olefin is carried out therein in order to form a second portion of the oxirane,
- a medium comprising the second portion of oxirane formed, solvent, unconverted olefin, unconsumed peroxide compound and possibly by-products is removed from this second reactor,
- the medium is introduced into another distillation column (A'),
- a second mixture containing the majority of the oxirane formed and unconverted olefin, solvent, water and possibly by-products is collected at the top of column (A'),
- a second medium depleted in oxirane, containing solvent, unconverted olefin, unconsumed peroxide compound and possibly by-products, is collected at the bottom of column (A'),
- each of the first and second mixtures containing the majority of the oxirane formed and the unconverted olefin is introduced into a condenser to separate out some of the unconverted olefin,
- a mixture depleted in unconverted olefin is removed in liquid form from each condenser,
- the liquid mixture is introduced into a second distillation column (B),

- a mixture of solvent and water is collected at the bottom of column (B) and is recycled into the first reactor, and
- an oxirane-based medium is collected at the top of column (B).

9. Process according to Claim 8, in which all of the peroxide compound is introduced into the first reactor.

10. Process according to Claim 8 or 9, in which:

- a third portion of the olefin, the second medium collected at the bottom of column (A') and optionally a third portion of the peroxide compound are introduced into a third reactor,
- an epoxidation of the third portion of olefin is carried out therein in order to form a third portion of the oxirane,
- a medium comprising the third portion of oxirane, the solvent, the unconverted olefin, possibly the unconsumed peroxide compound and possibly by-products is removed from this third reactor,
- this medium is introduced into yet another distillation column (A"),
- a medium is collected at the top of column (A") and is recycled, after condensation, into the first reactor,
- an aqueous effluent is collected at the bottom of column (A").

11. Process according to any one of Claims 1 to 9, in which the oxirane is propylene oxide, the olefin is propylene, the peroxide compound is hydrogen peroxide, the solvent is methanol and the catalyst contains TS-1.