

This invention relates to an improved process for the production of hydrogen peroxide by the anthraquinone method.

5 In the so-called anthraquinone method (cf. the comprehensive account in Ullmanns Enzyklopädie der technischen chemie, 4th revised and extended Edition, Vol. 17, pages 697-704), an anthraquinone derivative, the reaction support, is dissolved in a solvent or solvent mixture and the working solution obtained is hydrogenated in the presence
10 of a catalyst. Part of the anthraquinone derivative is converted into the corresponding anthrahydroquinone derivative. After the hydrogenation catalyst has been filtered off, the working solution is aerated with oxygen or an oxygen-containing gas (generally air), the anthraquinone
15 derivative being reformed with formation of hydrogen peroxide.

After extraction of the hydrogen peroxide dissolved in the working solution with water, the working solution can be returned to the hydrogenation stage. Constant repetition
20 of the individual phases results in a cyclic process in which hydrogen peroxide is synthesized from the gases hydrogen and oxygen.

Irrespective of the apparatus used for extraction of the hydrogen peroxide, two phases are always obtained after
25 the extraction stage, namely the working solution phase (raffinate) of depleted H_2O_2 content and the aqueous hydrogen peroxide phase (extract).

Each phase contains small amounts of the other phase in very finely dispersed form, i.e. the working solution
30 phase contains very fine droplets of a dilute aqueous hydrogen peroxide while small quantities of working solution droplets are dispersed in the aqueous hydrogen peroxide phase.

To separate the aqueous dispersed phase, the working
35 solution phase is normally passed through commercial

coagulators and separators, so-called "water separators". The phase separated in the "water separators" is a dilute aqueous hydrogen peroxide solution.

5 Several measures have already been proposed for purification of the aqueous hydrogen peroxide extract.

For example, the aqueous H_2O_2 solutions can be purified by adsorptive treatment. The following adsorbents have already been proposed: active carbon (US-PS 2,919,975), active carbon in the form of finely divided charcoal, MgO, 10 freshly precipitated $Al(OH)_3$ or $Mg(OH)_2$ (GB-PS 817,556), an active carbon partly deactivated by adsorption of organic substances inert to H_2O_2 (DE-PS 15 67 814), ethylene polymers having a molecular weight above 2,000 (GB-PS 794,433), water-insoluble, solid, non-polymeric organic 15 substances having molecular weights in the range from about 170 to 1,000 (DE-PS 11 08 191) and porous synthetic resins which are free from chemical functions (17 92 177).

Since active carbon decomposes the hydrogen peroxide to be purified, the treatment is preferably carried out at 20 low temperatures. In addition, the adsorbents become laden with the impurities as the purification process progresses and have to be regenerated with solvents in a separate circuit.

It is also known (US-PS 3,043,666 - FMC) that the 25 aqueous H_2O_2 solution may initially be treated with a selective solvent for quinones and the raffinate obtained subsequently heated in the presence of a stabilizer until coloration occurs. The dissolved organic constituents have been oxidized by hydrogen peroxide and are then retreated 30 by extraction and finally distilled. These measures are so elaborate that their application is only justified in the case of special qualities.

In other purification processes, the aqueous hydrogen peroxide extract is extracted with a solvent. The solvent 35 used may be an inert liquid hydrocarbon having a boiling

point under atmospheric pressure of not more than 145°C (DE-AS 10 36 225) or a hydrocarbon having boiling points in the range from 50 to 120°C and solubilities in water of less than 0.1% (JP-PS 35-2361). Even certain chlorinated hydrocarbons have been proposed (DE-AS 11 35 866). In the extractive purification processes which use a low-boiling solvent, solvent residues have to be stripped from the H₂O₂ after purification, in addition to which the impurity-laden solvent has to be regenerated in a separate circuit, i.e. expensively. Finally, many of the proposed solvents have a low flash point.

The disadvantages mentioned above are said to be avoided if the purification step is carried out in a solvent mixture consisting of aromatic hydrocarbons boiling at temperatures of 145 to 200°C (GB-PS 841,323).

It is also known that a mixture of aromatic hydrocarbons having a boiling point above 145°C and methyl cyclohexyl acetate in certain ratios can be used for purification of the crude aqueous hydrogen peroxide solutions (DE-AS 14 67 091).

In the prior art, extraction of the impurities is carried out in spray columns, in sieve plate columns or packed columns by the countercurrent method. Entrained solvent droplets are removed from the aqueous phase in a following holding zone.

It is known that, although the transfer of material in an extraction process increases with increasing phase interface, separation of a two-phase mixture on the other hand is easier, the larger the droplets of the dispersed phase. The effect of these two conflicting facts is to limit the result of extractive purification of aqueous hydrogen peroxide solutions with solvents in columns.

FR-A 1 234 731 describes a process for purification of the working solution to avoid an increase in the content of non-volatile carbon in the hydrogen peroxide extract which,

in some cases, can occur during the continuous cyclic process. Purification comprises washing the working solution with water, preferably after extraction of the hydrogen peroxide from the oxidized working solution. This washing process, which is carried out on the lines of an extraction, enables the yield of hydrogen peroxide to be increased and the content of non-volatile carbon in the crude H_2O_2 extract to be returned to or kept constant at a limit value specific to the process.

FR-A 1 492 339 relates to the coalescence of emulsions from the working solution and water in the process for the production of hydrogen peroxide. The two phases of the emulsion are separated in coalescers which are made up of a microporous layer of glass fibres and a wide-mesh layer of polyethylene, polypropylene or polytetrafluoroethylene for droplet enlargement.

The problem addressed by the present invention was to post-purify the solutions accumulating after the extraction stage, i.e. the hydrogen-peroxide-depleted working solution and the aqueous hydrogen peroxide extract, in order to increase the yield of hydrogen peroxide and to reduce the carbon content and the colour value of the hydrogen peroxide. The measures to be taken would avoid problems caused by moisture in the working solution during operation of the process. In addition, a clouded hydrogen peroxide solution obtained in the event of disrupted extraction would be able to be converted into a product of high quality.

A process has been found for the production of hydrogen peroxide by the so-called anthraquinone method, the hydrogen-peroxide-depleted working solution obtained during the extraction with water, which still contains small quantities of dilute aqueous hydrogen peroxide solution in very fine dispersion, and the hydrogen peroxide extract, which still contains small quantities of working solution in very fine dispersion, being subsequently purified by

separation of the particular dispersed phase from the other phase using coalescers which contain one or more filter layers of glass fibres, have a droplet-enlarging structure and are arranged in a separator unit, the process being
5 characterized in that 1 to 5% by volume water or a low-concentration aqueous hydrogen peroxide solution, based on the hydrogen-peroxide-depleted working solution, are added to the hydrogen-peroxide-depleted working solution and 0.5 to 5% by volume of a solvent mixture consisting of known
10 quinone solvents for the anthraquinone method, based on the hydrogen peroxide extract, are added to the hydrogen peroxide extract before entry into the coalescer stage, followed by mixing and the coalescers contain glass-fibre filter layers of thermally desized glass fibre filament
15 yarn.

Both phases accumulating after extraction with water, i.e. the working solution (raffinate) and the aqueous hydrogen peroxide solution (extract) are treated in accordance with the invention.

20 As mentioned, aqueous hydrogen peroxide solution may also be added to the working solution in addition to water. The aqueous hydrogen peroxide solutions added will preferably have low concentrations. In a particularly preferred embodiment, water is added to the working solution and,
25 after dispersion, the dispersed aqueous phase is separated from the working solution by means of coalescers. Water or aqueous hydrogen peroxide solutions are added to the working solution in quantities of 1 to 5% by volume, based on the working solution. In a particularly preferred
30 embodiment, water is added in a quantity of 1 to 3% by weight based on the working solution.

In principle, any of the quinone solvents typically used in the anthraquinone method may be used as constituents of the solvent mixture to be added to the hydrogen peroxide
35 extract. Quinone solvents are understood to be both pure

substances known for this purpose and also mixtures thereof. In many cases, the quinone solvent already present in the working solution will be selected. A mixture of aromatic benzines boiling at temperatures in the range from
5 180 to 220°C have proved to be a particularly suitable quinone solvent.

The solvent mixture is used in quantities of 0.5 to 5% by volume, based on the hydrogen peroxide extract. In a particularly preferred embodiment, the quinone solvent is
10 added in a quantity of 1 to 3% by volume, based on the hydrogen peroxide extract.

Both the aqueous phase and the organic solvent mixture are added to the raffinate or hydrogen peroxide extract accumulating after the extraction stage and are mixed
15 therewith in standard mixers. Intensive mixing is preferred.

The most favourable degree of dispersion of the added phase, which is dependent *inter alia* upon the structure and filtration fineness of the coalescers used, may readily be
20 determined by preliminary tests.

The particular dispersed phase is then separated by means of coalescers mounted in a suitable separator unit. Like the other parts of the apparatus, these coalescers are made of a material which is resistant to hydrogen peroxide.
25 One, two or more coalescers may be used. Two or more coalescers are arranged in tandem in crosscurrent or countercurrent.

Coalescers used in accordance with the invention are understood to be those of the type described, for example,
30 in Chemical Engineering Progress, Vol. 59, No. 9, pages 87 to 88 (1963) and in GB-PS 1,427,704. These coalescers have a droplet-enlarging structure and contain one or more filter layers of thermally desized glass fibre filament yarn. The most favourable loading of the coalescers, i.e.
35 the throughput of dispersion per unit of time and filter

element, is best determined by the expert in preliminary tests.

5 The process according to the invention is carried out at temperatures of 10 to 70°C although it may also be carried out at higher or lower temperatures. The process according to the invention is preferably carried out at 20 to 50°C. According to the invention, the raffinate and the H₂O₂ extract may be treated at different temperatures.

10 By the basically paradoxical measure of wanting to dissolve the dispersed phase substantially completely out of the raffinate and/or extract by repeated controlled addition of this phase, the degree to which, on the one hand, hydrogen peroxide and, on the other hand, impurities which would lead to coloration and to an excessive carbon
15 content of the hydrogen peroxide are respectively washed out of the raffinate and the extract is considerably increased. The yield and also the colour and carbon content of the hydrogen peroxide are considerably improved by the process according to the invention (Examples 2 and
20 4).

By increasing the dispersed aqueous phase in the raffinate, i.e. in the working solution, with subsequent separation of the dispersed phase by the coalescer(s), it is possible both to increase the total yield of hydrogen
25 peroxide and to prevent an increase in the relative moisture content of the working solution, see Examples 3 and 4. However, it was precisely the increase in the moisture content of the raffinate which was always regarded as highly disruptive. The result achieved in accordance with
30 the invention, i.e. keeping the moisture content constant during operation, was not foreseeable.

The relative moisture content is understood to be the ratio expressed in percent of the moisture actually present in the continuous recycled working solution to the saturation
35 content of the pure working solution corresponding to

the prevailing temperature.

The invention is illustrated by Examples 1 to 4. The same reaction support, namely a mixture of 2-ethyl anthraquinone and 2-ethyl tetrahydroanthraquinone, and the same
5 working solution containing trioctyl phosphate as hydroquinone solvent and an aromatic benzine boiling at 185 to 205°C as quinone solvent are used in all the Examples.

Example 1

10 (Comparison Example according to the prior art)

In a plant for the production of hydrogen peroxide by the anthraquinone method, a packed column in which hydrogen peroxide and the quinone solvent of the working solution are moved in countercurrent to one another is in operation
15 for purification of the aqueous hydrogen peroxide leaving the extraction stage. As the dispersed phase, the aqueous hydrogen peroxide phase flows downwards through the column while the quinone solvent, as the continuous phase, is passed upwards through the column.

20 The efficiency of purification is determined through the reduction in the carbon content in mg C/l crude aqueous H_2O_2 product and, given uninterrupted operation of the plant, amounts on average to 30 mg C/l H_2O_2 for an initial value of 220 mg C/l aqueous crude H_2O_2 product.

25 Disruptions occasionally occurring in the plant lead to a crude product which is opal to slightly clouded in appearance. In this case, the clouding cannot be eliminated by the purification stage, i.e. the product obtained after the purification stage requires further treatment.
30 In addition, dissolved chromophores give the hydrogen peroxide a very slightly yellowish colour which indicates a colour value of 3 in a standard colour value test. To determine the colour value, calibrating solutions of $FeCl_3$ in distilled water are prepared in accordance with the
35 following scale:

	Colour value	mg FeCl ₃ /l
	0	54.0
	1	162.6
	2	270.4
5	3	378.6

The hydrogen peroxide sample and the FeCl₃ solutions are then compared for colour in glass tubes.

10 **Example 2**

A partial stream of the aqueous hydrogen peroxide leaving the extraction stage of the plant described in Example 1 is passed through a coalescer stage consisting of two coalescer elements arranged in tandem and each containing a filter layer of thermally desized glass fibre filament yarn and layers for droplet enlargement. 2 Parts by volume of an aromatic benzine boiling at 182 to 214°C to 100 parts by volume hydrogen peroxide extract are added in countercurrent to the hydrogen peroxide phase flowing off from the extraction stage, the two phases are thoroughly mixed by a speed-controlled pump and are separated in the coalescer elements at a temperature of 20 to 25°C.

The efficiency of the stage, again expressed in mg C/l H₂O₂, amounts to 100 - 120 mg C/l H₂O₂ in relation to the same original C content as in Example 1. The colour value, as measured on the FeCl₃ scale, falls to 0 - 1. Despite occasional malfunctions in the extraction stage of the plant, as a result of which a clouded product is obtained, complete separation always takes place in the coalescer stage, i.e. the hydrogen peroxide leaving the coalescer stage is always of the same high quality.

Example 3 (Comparison Example)

In the plant described in Example 1, the working solution (raffinate) leaving the extraction stage is passed

without previous addition of the dispersed phase through a so-called water separator equipped with coalescer elements in order to separate the dilute aqueous hydrogen peroxide phase dispersed therein. Each time the unit fitted with new elements is brought into operation, almost 100% separation of the dispersed aqueous phase is achieved, i.e. the moisture content of the working solution after the water separation stage amounts to 100 - 102% relative moisture. With time, however, the moisture content of the working solution slowly increases beyond the initial value, i.e. the working solution contains a certain amount of non-separated dispersed aqueous phase. After about 1 year, a value of approx. 150 to 180% relative moisture is obtained so that the coalescer elements have to be removed and replaced by new elements.

Occasional malfunctions in the extraction stage, which lead to an increase in the accumulation of dispersed aqueous phase in the working solution, briefly produce an increase in the relative moisture to 300%, depending on the extent of the malfunction.

Example 4

In the plant described in Example 1, approx. 2% by volume water, based on the working solution, is introduced into and intensively mixed with the working solution (raffinate) before it enters the coalescer stage. Over an operating period of 12 months, a relative moisture content of 100% is constantly observed in the working solution leaving the coalescer stage. By working up the aqueous phase separated off, which contains a little hydrogen peroxide, the H_2O_2 yield increases by 0.2 to 0.3%. A relative moisture content of 100% is always found in the working solution after the coalescer stage, even despite occasional malfunctions in the extraction stage. This excellent performance of the separation stage was observed even after operation for more than 18 months.

**CLAIMS**

1. A process for the production of hydrogen peroxide by the so-called anthraquinone method, the hydrogen-peroxide-depleted working solution obtained during the extraction with water, which still contains small quantities of dilute aqueous hydrogen peroxide solution in very fine dispersion, and the hydrogen peroxide extract, which still contains small quantities of working solution in very fine dispersion, being subsequently purified by separation of the particular dispersed phase from the other phase using coalescers which contain one or more filter layers of glass fibres, have a droplet-enlarging structure and are arranged in a separator unit, characterized in that 1 to 5% by volume water or a low-concentration aqueous hydrogen peroxide solution, based on the hydrogen-peroxide-depleted working solution, are added to the hydrogen-peroxide-depleted working solution and 0.5 to 5% by volume of a solvent mixture consisting of known quinone solvents for the anthraquinone method, based on the hydrogen peroxide extract, are added to the hydrogen peroxide extract before entry into the coalescer stage, followed by mixing and the coalescers contain glass-fibre filter layers of thermally desized glass fibre filament yarn.
2. A process as claimed in claim 1, characterized in that 1 to 3% by volume water, based on the hydrogen-peroxide-depleted working solution, are added to the depleted working solution.
3. A process as claimed in claim 1 or 2, characterized in that 1 to 3% by volume quinone solvent, based on the hydrogen peroxide extract, are added to the aqueous hydrogen peroxide extract.
4. A process as claimed in one or more of claims 1 to 3, characterized in that two coalescers arranged in tandem are used to purify the hydrogen peroxide extract and the hydrogen-peroxide-depleted working solution.