

Process for the preparation of an ultrapure hydrogen peroxide solution by ion exchange in the presence of acetate ions

5 The use of hydrogen peroxide for advanced technology applications or applications in the food industry, in hygiene or health requires increasingly pure products which must meet a growing number of increasingly tight specifications. In particular, the demands of users are turning towards hydrogen peroxide solutions in which the content of each metal impurity is less than one part per billion (ppb) and preferably less than 500 parts per trillion (ppt). In the following account, such solutions will be known as
10 ultrapure hydrogen peroxide solutions.
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 It is well known, according to the prior art, that it is possible to remove certain impurities by passing the solution through a bed of ion-exchange adsorbents. Mention may be made, for example, of
20 functionalized polymers of polystyrene/divinylbenzene type, silicas or aluminosilicates, in particular the varieties containing controlled micropores, such as zeolites or active charcoals; these solids carry functional groups capable of complexing either cations or anions. Mention may be made, as examples of
25 functional groups capable of complexing cations, of the carboxylic, sulphonic, phosphonic, hydroxide, amine oxide or phosphine oxide groups or alternatively of cyclic or open polyoxaalkyls, such as, for example, ethylene oxide polymers. Mention may be made, as
30 examples of functional groups capable of complexing anions, of the quaternary ammonium or quaternary phosphonium groups. These adsorbents can also be obtained by polymerization of a monomer carrying a
35 functional group, for example poly(methacrylic acid)s, poly(vinylphosphonic acid)s, polyvinylpyridines, polyvinylpyrrolidones, poly(vinyl alcohol)s, saponified polylactones and copolymers containing these units. The adsorbents which are the most often described are

polystyrene gels or crosslinked polystyrenes possessing sulphonic $-SO_3H$ or trimethylammonium $(CH_3)_3N^+$ functional groups.

Many combinations have been provided, such as,
5 for example, anionic resin followed by cationic resin or cationic resin followed by anionic resin or alternatively anionic resin followed cationic resin followed by cationic + anionic "mixed bed". Additions to the inter-stage phases are also described, such as,
10 for example, the addition of acid in order to modify the pH or the addition of chelating agents, such as aminomethylenecarboxylic or aminomethylenephosphonic derivatives.

It is well known to the person skilled in the
15 art that the use of anion-exchange adsorbents presents great difficulties when employed for the purification of hydrogen peroxide. In particular, the hydroxide form, under which these products are generally available industrially, cannot be used directly because
20 of its excessively high basicity, resulting in significant decomposition of hydrogen peroxide. Many publications describe the use of adsorbents exchanged by carbonate or bicarbonate ions, which are less basic, in order to limit the decomposition of hydrogen
25 peroxide, without, however, eliminating it completely.

It is essential to be able to control this phenomenon of decomposition of hydrogen peroxide on adsorbent beds because, as this decomposition with release of gaseous oxygen is exothermic, the rate is
30 accelerated according to the well known Arrhenius law. The formation of a gas pocket can further aggravate the phenomenon since, by separating the liquid from the decomposition point, the heat released can no longer be removed by evaporation of the water and the cooling
35 effect of the liquid is lost. Such a process is characteristic of a divergent reaction which can result in an extremely violent autoaccelerated decomposition reaction, which is all the more dangerous since it is

highly exothermic and produces gaseous oxygen, thus with a considerable expansion force which can cause explosions.

5 The object of the present invention is thus to obtain ultrapure hydrogen peroxide solutions while limiting the risk of violent decomposition of the hydrogen peroxide during the purification stages.

The subject of the present invention is a process for the preparation of an ultrapure hydrogen peroxide solution, characterized in that:

10 a) it comprises at least one sequence which includes passing the solution to be purified through at least one bed of anion-exchange adsorbents (AEA) and at least one bed of cation-exchange adsorbents (CEA)

15 b) at least one bed of anion-exchange adsorbents contains carboxylate ions of formula $R-COO^-$ in which R represents a hydrogen atom, an aryl radical containing from 6 to 10 carbon atoms or an alkyl radical containing from 1 to 4 carbon atoms, the said aryl and
20 alkyl radicals being either unsubstituted or substituted by one or more fluorine atoms, and

c) the first (AEA) bed which the solution to be purified passes through is a bed containing carboxylate ions of formula $R-COO^-$.

25 Carboxylate ion of formula $R-COO^-$ is understood to mean in particular the trifluoroacetate ion or the benzoate ion, the formate ion, the acetate ion or the fluoroacetate ion, and preferably the acetate ion.

30 The hydrogen peroxide solution to be purified according to the present invention is a technical aqueous solution having a concentration of 1 to 70% by weight and preferably of 5 to 50% by weight. The adsorbents are chosen from those which are described above.

35 The beds of adsorbents each exhibit a height to diameter ratio of between 0.5 and 50, preferably greater than 3, in particular between 5 and 10 and more particularly of 6.

The hydrogen peroxide solution throughputs, expressed as volume of solution/hour passed per volume of bed of adsorbent, can vary between 0.5 and 100, preferably from 1 to 50 and more particularly from 10 to 30.

The anion-exchange adsorbents will preferably be fed in an upward mode, whereas the beds of cation-exchange adsorbents will preferably be fed in a downward mode. It is possible to define the geometries of the beds so that the true space velocities and/or throughputs in each adsorbent are optimized.

It is also possible to operate under pressure; a working pressure of less than 5 atmospheres above atmospheric pressure will preferably be chosen.

The temperature of the solution to be purified according to the process as described above is less than or equal to 30°C and preferably between -10°C and +10°C.

In a preferred alternative form of the process as defined above, the sequence for passing the solution to be purified through the ion-adsorbing beds begins with passage through a bed of anion adsorbents (AEA) and continues with passage through a bed of cation adsorbents (CEA).

In another alternative form of the process as defined above, the process comprises, upstream or downstream of sequences for passing the solution to be purified through the beds of ion-exchange adsorbents, one or more purification stages, such as, for example, distillation, liquid extraction, crystallization, absorption, filtration, ultrafiltration, nanofiltration or reverse osmosis. If appropriate, the starting solution is brought beforehand to the desired assay and then purified. Depending on the degree of purity and of dilution of the hydrogen peroxide solution to be purified, one or more of these additional stages is/are employed.

In a first preferred alternative form of the present invention, the technical hydrogen peroxide solution to be purified, which is at a concentration of 30% to 70% by weight, is distilled and brought to the
5 desired assay beforehand and then purified through at least two beds of ion-exchange adsorbents, according to the sequence which is the subject of the present invention.

According to a second alternative form of the
10 purification process which is the subject of the present invention, a hydrogen peroxide solution of technical quality or of so-called "food" quality, having a concentration of approximately 50 to 70% by weight, is subjected to the following pretreatment: a
15 first distillation/concentration stage, in order to obtain a condensate having a concentration of greater than 80%, plus a first purification by low-temperature crystallization and the removal of the supernatant. The crystals collected are washed, superficially dried and
20 then melted and the solution obtained is diluted to 30 or 35% with deionized water of ultrapure electronic quality.

In a third preferred alternative form of the present invention, in particular if the carbon content
25 of the hydrogen peroxide solution is a constraint forming an integral part of the required specifications, a second bed of anion-exchange adsorbents can be added to the purification line in order to retain the carboxylate ions released by the
30 complexation of the metal impurities in the first bed of anion-exchange adsorbents.

It is thus possible very easily to obtain, from an ordinary technical quality, a hydrogen peroxide solution of "electronic" quality containing less than
35 200 ppt of each of the metal cations from groups IA to VIIA (with the exception of oxygen) and from groups IB to VIII of the table of the Periodic Classification of the Elements.

Mention may be made, by way of illustration of the purification process which is the subject of the present invention, of, for example, the series of sequences: AEA (acetate)/CEA/AEA (bicarbonate or carbonate)/CEA.

Another subject of the invention is a plant for the implementation of the process as defined above.

In a preferred alternative form of the present plant, the beds of anion-exchange adsorbents are fed in upward mode and the beds of cation-exchange adsorbents are fed in downward mode.

In another preferred alternative form of the plant, the latter is situated on the customer's site, such as, for example, a site for the manufacture of electronic components, and connected directly to the point of use of the hydrogen peroxide by the said customer. In this alternative form, the hydrogen peroxide solution to be purified can originate from a storage tank situated on the same site, or alternatively is manufactured on this same site by virtue of a so-called "on site" production unit.

The following examples illustrate the invention without, however, limiting it.

EXAMPLE A : Stability study

It has been shown that the phenomenon of initiation of a violent decomposition reaction by simple heating of a bed of anion-exchange resin in the trimethylammonium bicarbonate form (Dowex A 550 UPE) in the presence of a 30% aqueous hydrogen peroxide solution at moderate temperature, for example 30 to 35°C, for a few tens of minutes is much faster with a resin which has been used for the purification of the peroxide than with a freshly exchanged resin. If the "TMR" (time to maximum rate), which indicates, at a given temperature, the induction period before initiation of the explosive decomposition, is taken as

evaluation parameter, the following results were obtained:

fresh resin:

5 T=56°C: TMR=15 min; T=51°C: TMR=30 min; T=44°C: TMR=60 min

used resin:

T=41°C: TMR=15 min; T=35°C: TMR=30 min; T=32°C: TMR=60 min

10 It is thus obvious that a used resin is much more sensitive to hydrogen peroxide autodecomposition phenomena, probably because of the catalytic effect of the metal species exchanged during purification.

Under the same conditions, no decomposition phenomenon is observed when an anion-exchange resin in the acetate form is heated for 12 hours at 45°C in the presence of a 30% aqueous hydrogen peroxide solution.

EXAMPLE B :

20 a) Comparative Example

A purification unit contains two columns filled respectively with 3 litres of an anion-exchange resin Dowex Monosphere A 550 UPE, which has been exchanged beforehand with a sodium bicarbonate solution and washed with water, and 3 litres of a cation-exchange resin Dowex Monosphere C 650 UPN. The diameter of the columns is approximately 11.7 centimetres, which gives a height of 28 centimetres. 900 litres of a 30% by weight aqueous hydrogen peroxide solution (solution A), obtained by diluting a 60% by weight commercial solution with ultrapure water, are introduced with a throughput of 130 litres per hour, in upward mode, into the first column charged with an (AEA) bed and then, in downward mode, into the second column charged with a (CEA) bed. The solution B is obtained.

b) Example according to the invention

The purification operation is carried out as in the preceding example, from a fresh sample of 900 litres of solution A, but by exchanging the anion-exchange resin Dowex Monosphere A 500 UPE beforehand with a sodium acetate solution.

The solution C is obtained.

Analysis of these three solutions for the purpose of determining the concentrations, expressed in ppt, of the main contaminants leads to the following results:

	Solution A	Solution B	Solution C
Na	675,000	55	26
Ca	1700	85	21
Fe	900	40	70
Ni	350	15	6
Cr	200	7	2
Cu	44	6	7
Mn	30	0.5	0.3

The preceding examples demonstrate that the decomposition of hydrogen peroxide on an (AEA) bed in the acetate form is much lower than that observed on a resin exchanged in the (bicarbonate or carbonate) form; they also demonstrate that the elements capable of decomposing H_2O_2 , namely Fe, Ni, Cr, Cu and Mn, are completely retained on this same (AEA) bed.

CLAIMS

1. Process for the preparation of an ultrapure hydrogen peroxide solution, characterized in that it comprises at least two successive sequences, the first of which includes passing the hydrogen peroxide solution to be purified through a bed of anion-exchange adsorbents containing acetate carboxylate ions of formula $R-COO^-$, followed by passing through a bed of cation-exchange adsorbents, and the second of which includes passing through a bed of anion-exchange adsorbents containing bicarbonate or carbonate ions and passing through a bed of cation-exchange adsorbents.

2. Process as defined in Claim 1, in which the $R-COO^-$ ion is the formate ion, the acetate ion, the fluoroacetate ion, the trifluoroacetate ion or the benzoate ion, and preferably the acetate ion.

3. Process as defined in one of Claims 1 or 2, comprising, upstream and/or downstream of the sequence for passing the solution to be purified through the beds of ion-exchange adsorbents, one or more purification stages, such as distillation, liquid extraction, crystallization, absorption, filtration, ultrafiltration, nanofiltration or reverse osmosis, and, if desired, a prior operation in which the starting solution to be purified is brought to the desired assay.

4. Process as defined in Claim 3, in which the technical hydrogen peroxide solution to be purified, which is at a concentration of 30% to 70% by weight, is distilled and brought to the desired assay beforehand.

5. Process as defined in Claim 3, in which a hydrogen peroxide solution of technical quality or of so-called "food" quality, having a concentration of approximately 50 to 70% by weight, is subjected to the following pretreatment: a first distillation/concentration stage, in order to obtain a condensate having a concentration of greater than 80%,



plus a first purification by low-temperature crystallization and the removal of the supernatant. The crystals collected are washed, superficially dried and then melted and the solution obtained is diluted to 30
5 or 35% with deionized water of ultrapure electronic quality.

6. Process according to one of Claims 1 to 5, characterized in that each of the beds of adsorbents exhibits a height to diameter ratio of greater than 3,
10 in particular between 5 and 10 and more particularly of

7. Plant for the implementation of the process as described in one of Claims 1 to 6, characterized in that it is situated on the site of use of the ultrapure hydrogen peroxide solution and in particular on the
15 site for the manufacture of electronic components.

8. Plant as described in Claim 7, in which the beds of anion-exchange adsorbents are fed in upward mode and the beds of cation-exchange adsorbents are fed in downward mode.