

PROCESS FOR PRODUCING A HIGH PURITY AQUEOUS SOLUTION OF HYDROGEN PEROXIDE

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for purifying an aqueous solution of hydrogen peroxide containing inorganic impurities safely and producing an aqueous solution of hydrogen peroxide having a very high purity with stability. The aqueous solution of hydrogen peroxide purified in accordance with this process is particularly used in the production of semiconductors and in the medical field.

2. Description of the Related Arts

Hydrogen peroxide has been produced mainly in accordance with the autoxidation process. Aqueous solutions of hydrogen peroxide produced in accordance with this process contain various inorganic impurities. An aqueous solution of hydrogen peroxide having a substantially practical concentration, i.e., 5 to 70% by weight, generally contains several hundreds $\mu\text{g/liter}$ of inorganic impurities. On the other hand, an aqueous solution of hydrogen peroxide containing residual inorganic impurities in an amount of several hundredths $\mu\text{g/liter}$ or less is required in recent years in the production of semiconductors.

As the process for purifying an aqueous solution of hydrogen peroxide by removing inorganic impurities contained, processes in which an ion exchange resin is brought into contact with the aqueous solution of hydrogen peroxide have been known. Examples of such processes include processes disclosed in the specifications of Japanese Patent Publication No.

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Showa 35(1960)-16677, German Patent Application Laid-Open No. 4214075, French Patent No. 2677011, Japanese Patent Application Laid-Open No. Heisei 5(1993)-17105, German Patent Application Laid-Open No. 4222109, and Japanese Patent Application Laid-Open No. Heisei 7(1995)-172805.

In the purification of an aqueous solution of hydrogen peroxide, a strong acidic cation exchange resin of a hydrogen type which comprises a copolymer of styrene and divinylbenzene as the base component and a sulfonic group as the ion exchange group and a strong basic anion exchange resin of a carbonate type, a bicarbonate type or a hydroxide type which comprises a copolymer of styrene and divinylbenzene as the base component and a quaternary ammonium group as the ion exchange group are generally used.

A cation exchange resin is used as an important agent to remove cationic species derived from metals and metal compounds contained in an aqueous solution of hydrogen peroxide. However, metals are contained not only as cations but also as anions, such as ions of metal oxides. Anionic species such as the anions of metals, chlorine ion and sulfate ion cannot be removed with a cation exchange resin.

In contrast to the cation exchange resin, an anion exchange resin is effective for removing metal compounds in the form of anions and other anionic species. However, cationic species cannot be removed with an anion exchange resin.

Therefore, an aqueous solution of hydrogen peroxide is purified with a cation exchange resin and an anion exchange resin successively in this order or in the reverse order. An aqueous solution of hydrogen peroxide



can also be purified by bringing the solution into contact with a mixture of a cation exchange resin and an anion exchange resin.

However, when an aqueous solution of hydrogen peroxide is purified in accordance with the above processes, chromium and iron are left remaining in the purified solution in larger amounts than those of other metals, and this situation causes a problem in the production of a high purity aqueous solution of hydrogen peroxide required in the field of semiconductors. It is not easy to purify an aqueous solution of hydrogen peroxide to such a level that the content of each metal impurity is several hundredths ppb.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an aqueous solution of hydrogen peroxide having a very high purity from an aqueous solution of hydrogen peroxide containing inorganic impurities which comprises metals and metal compounds.

The present invention has been completed as the result of intensive studies by the present inventors on a process for purification of an aqueous solution of hydrogen peroxide using an ion exchange resin.

Accordingly, the present invention provides a process for producing a high purity aqueous solution of hydrogen peroxide which comprises bringing an aqueous solution of hydrogen peroxide into contact with a strong acidic cation exchange resin of a hydrogen type which comprises a copolymer of styrene and divinylbenzene as the base component and sulfonic group as the exchange group and is a porous type having a degree of crosslinking of 6 to 10 or a gel type having a degree of crosslinking of 6 to



8.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The resin used in the present invention comprises a copolymer of styrene and divinylbenzene as the base component. The copolymer is obtained by copolymerization of a mixture of styrene monomer and divinylbenzene monomer and has a steric network structure in which flexible styrene chains are crosslinked with divinylbenzene units. The larger the relative amount of divinylbenzene in the copolymerization, the tighter the network structure. The smaller the relative amount of divinylbenzene in the copolymerization, the looser the network structure. Thus, the content of crosslinking varies depending on the relative amount of divinylbenzene used, and tightness of the network structure also varies depending on the relative amount of divinylbenzene. A degree of crosslinking is defined as the fraction (% by weight) of divinylbenzene monomer in the total amount of the monomers used.

The cation exchange resin of the gel type is an ion exchange resin which contains micropores, is almost transparent and has a gel structure. The cation exchange resin of the porous type is essentially the same as the cation exchange resin of the gel type except that the cation exchange resin of the porous type contains macropores which are physically formed and is opaque. The cation exchange resin of the porous type is referred to differently by each manufacturer. For example, the resin is referred to as a resin of the porous type by MITSUBISHI CHEMICAL Co., Ltd. and as a resin of an MR type (Macro-reticular type) by ORGANO Co., Ltd.

When a cation exchange resin has a small degree of crosslinking,

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elution of metal impurities from the resin itself is small. However, such a resin has a small selectivity coefficient and is not advantageously used for the purification because there are some metal species which are not easily removed. Moreover, the contact with hydrogen peroxide which is an oxidizing agent for a long period of time causes irreversible swelling of the resin to decrease the physical strength. Therefore, such a resin is not advantageous in the practical application.

On the other hand, when a cation exchange resin has a large degree of crosslinking, elution of metal impurities from the cation exchange resin itself increases although the exchange volume and the selectivity coefficient increase and the physical strength is enhanced. Therefore, it is difficult to obtain an aqueous solution of hydrogen peroxide having a very high purity using such a cation exchange resin.

In general, a cation exchange resin is commercially available in the form of the sodium salt. Therefore, it is necessary that a commercially available cation exchange resin be converted into the hydrogen type before being used in the present invention. The agent used for this purpose is not particularly limited. A mineral acid such as hydrochloric acid and sulfuric acid is generally used.

The process for converting a cation exchange resin from the sodium salt type into the hydrogen type is not particularly limited. A batch process in which a cation exchange resin is dipped into an agent or a continuous process in which a column is packed with the cation exchange resin and an agent is passed through the column may be used. From the standpoint of the operability and the efficiency of the conversion, the continuous process is more effective. For example, a column is packed



with a cation exchange resin and a solution of an acid having a concentration of 0.1 to 10 N is passed through the column in an amount by equivalent 5 times the exchange volume of the cation exchange resin or more, and the resin is converted into the hydrogen type. The converted resin is washed with ultra-pure water and used for the purification of an aqueous solution of hydrogen peroxide. Before the conversion of the cation exchange resin into the hydrogen type with an acid, the resin may be washed with a solution of an acid, a solution of an alkali, an organic solvent, or a combination of these washing liquids in advance.

In the process of the present invention, an aqueous solution of hydrogen peroxide can be purified with a combination of the above cation exchange resin and an anion exchange resin. It is preferable that these ion exchange resins are used as a mixture. The ratio of the amount of the cation exchange resin to the amount of the anion exchange resin is 9:1 to 1:9, preferably 8:2 to 2:8, based on the exchange volume.

The anion exchange resin used in the above is a strong basic anion exchange resin which comprises a quaternary ammonium group as the exchange group and has been converted into the carbonate type, the bicarbonate type or the hydroxide type. In the present invention, when an aqueous solution of hydrogen peroxide is purified with a mixture of the ion exchange resins, the aqueous solution of hydrogen peroxide may be purified with a cation exchange resin alone, an anion exchange resin alone, or a combination of these ion exchange resins before the above purification. It is preferable that the mixture of the ion exchange resins is used in the final step of the purification.

The concentration of hydrogen peroxide in the aqueous solution



used for the purification is not particularly limited. An aqueous solution of hydrogen peroxide having a substantially practical concentration, i.e., 5 to 70% by weight, is used. The temperature during the purification of the aqueous solution of hydrogen peroxide is not particularly limited, either. A temperature in the range from the freezing point of the aqueous solution of hydrogen peroxide to 30°C is preferable because hydrogen peroxide is decomposed at a temperature over 30°C.

The process of bringing the aqueous solution of hydrogen peroxide into contact with the ion exchange resin is not particularly limited. A batch process in which the ion exchange resin is placed into the aqueous solution of hydrogen peroxide and the mixture is left standing or stirred together or a continuous process in which the aqueous solution of hydrogen peroxide is passed through a column packed with the ion exchange resin may be used. The continuous process is preferable from the standpoint of the operability and the degree of purification. As for the speed of passing the solution through the column, the SV (space velocity) is 1 to 500 hr⁻¹.

To summarize the advantages obtained by the present invention, an aqueous solution of hydrogen peroxide containing inorganic impurities such as metals and metal compounds can be purified, and an aqueous solution of hydrogen peroxide having a very high purity can be produced.

EXAMPLES

The present invention will be described with reference to the following Examples. However, the present invention is not limited to the Examples. The concentration of a metal was measured in accordance with the ICP-MS (Inductive Coupling-Mass Spectrometry).



Example 1

A 30% by weight aqueous solution of hydrogen peroxide containing 70 ppb by weight of aluminum, 5 ppb by weight of chromium and 4 ppb by weight of iron as impurities was purified by passing through a column packed with a strong acidic cation exchange resin of the porous type PK212 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 6; the hydrogen type) and a column packed with a strong basic anion exchange resin IRA900 manufactured by ORGANO Co., Ltd. (the bicarbonate type) successively at an SV of 200 hr⁻¹. The concentrations of the metals after the purification are shown in Table 1.

Example 2

The same aqueous solution of hydrogen peroxide as that used in Example 1 was purified in accordance with the same procedure as that in Example 1 except that a strong acidic cation exchange resin of the porous type PK220 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 10; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 1.

Example 3

The same aqueous solution of hydrogen peroxide as that used in Example 1 was purified in accordance with the same procedure as that in Example 1 except that a strong acidic cation exchange resin of the gel type SK1B manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of



crosslinking, 8; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 1.

Example 4

The same aqueous solution of hydrogen peroxide as that used in Example 1 was purified in accordance with the same procedure as that in Example 1 except that a strong acidic cation exchange resin of the gel type XT-1004 manufactured by ORGANO Co., Ltd. (degree of crosslinking, 6; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 1.

Comparative Example 1

The same aqueous solution of hydrogen peroxide as that used in Example 1 was purified in accordance with the same procedure as that in Example 1 except that a strong acidic cation exchange resin of the porous type PK208 manufactured by MITSUBISHI CHEMICAL Co. (degree of crosslinking, 4; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 1.

Comparative Example 2

The same aqueous solution of hydrogen peroxide as that used in Example 1 was purified in accordance with the same procedure as that in Example 1 except that a strong acidic cation exchange resin of the porous type 200C manufactured by ORGANO Co., Ltd. (degree of crosslinking, 20;



the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 1.

Comparative Example 3

The same aqueous solution of hydrogen peroxide as that used in Example 1 was purified in accordance with the same procedure as that in Example 1 except that a strong acidic cation exchange resin of the gel type SK104 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 4; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 1.

Comparative Example 4

The same aqueous solution of hydrogen peroxide as that used in Example 1 was purified in accordance with the same procedure as that in Example 1 except that a strong acidic cation exchange resin of the gel type SK110 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 10; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 1.

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Table 1 Concentration of metals in the purified aqueous solution of hydrogen peroxide

	Al (ppt by wt.)	Cr (ppt by wt.)	Fe (ppt by wt.)
Example 1	34	28	20
Example 2	24	31	24
Example 3	35	30	22
Example 4	31	34	29
Comparative Example 1	95	80	52
Comparative Example 2	102	120	71
Comparative Example 3	63	75	76
Comparative Example 4	63	71	52

Example 5

A 30% by weight aqueous solution of hydrogen peroxide containing 3 ppb by weight of aluminum, 2 ppb by weight of chromium and 0.5 ppb by weight of iron as impurities was purified by passing through a column packed with a mixture of a strong acidic cation exchange resin of the porous type PK212 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 6; the hydrogen type) and a strong basic anion exchange resin IRA900 manufactured by ORGANO Co., Ltd. (the



bicarbonate type) in a ratio by exchange volume of 6:4 at an SV of 200 hr⁻¹. The concentrations of the metals after the purification are shown in Table 2.

Example 6

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the porous type PK216 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 8; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Example 7

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the porous type PK220 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 10; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Example 8

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the gel type



SK1B manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 8; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Example 9

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the gel type XT-1004 manufactured by ORGANO Co., Ltd. (degree of crosslinking, 6; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Example 10

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the gel type IR-120B manufactured by ORGANO Co., Ltd. (degree of crosslinking, 8; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Comparative Example 5

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the porous type PK208 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree



of crosslinking, 4; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Comparative Example 6

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the porous type PK228 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 14; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Comparative Example 7

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the porous type 200C manufactured by ORGANO Co., Ltd. (degree of crosslinking, 20; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Comparative Example 8

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the gel type SK104 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of



crosslinking, 4; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

Comparative Example 9

The same aqueous solution of hydrogen peroxide as that used in Example 5 was purified in accordance with the same procedure as that in Example 5 except that a strong acidic cation exchange resin of the gel type SK110 manufactured by MITSUBISHI CHEMICAL Co., Ltd. (degree of crosslinking, 10; the hydrogen type) was used as the cation exchange resin. The concentrations of the metals after the purification are shown in Table 2.

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**Table 2 Concentration of metals in the purified aqueous solution of
hydrogen peroxide**

	Al	Cr	Fe
	(ppt by wt.)	(ppt by wt.)	(ppt by wt.)
Example 5	32	29	21
Example 6	23	28	19
Example 7	18	20	27
Example 8	27	31	13
Example 9	33	29	17
Example 10	20	11	24
Comparative Example 5	82	72	49
Comparative Example 6	68	90	69
Comparative Example 7	91	102	66
Comparative Example 8	62	71	70
Comparative Example 9	57	64	42

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WHAT IS CLAIMED IS:

1. A process for producing a high purity aqueous solution of hydrogen peroxide which comprises bringing an aqueous solution of hydrogen peroxide into contact with a strong acidic cation exchange resin of a hydrogen type which comprises a copolymer of styrene and divinylbenzene as a base component and sulfonic group as an exchange group, has a degree of crosslinking of 6 to 10 and is a porous type.
2. A process for producing a high purity aqueous solution of hydrogen peroxide which comprises bringing an aqueous solution of hydrogen peroxide into contact with a strong acidic cation exchange resin of a hydrogen type which comprises a copolymer of styrene and divinylbenzene as a base component and sulfonic group as an exchange group, has a degree of crosslinking of 6 to 8 and is a gel type.
3. A process according to Claim 1, wherein an anion exchange resin is mixed with the strong acidic cation exchange resin.
4. A process according to Claim 2, wherein an anion exchange resin is mixed with the strong acidic cation exchange resin.

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