DESCRIPTION

Title of the Invention: Method for producing a high-purity tetraalkylammonium hydroxide aqueous solution

Technical Field:

[0001]

The present invention relates to a method for producing a high-purity tetraalkylammonium hydroxide aqueous solution.

Background Art:

[0002]

Precision processing technology for microfabrication of miniaturized devices is becoming increasingly important in a wide range of fields, including the manufacturing of semiconductor integrated circuits such as LSIs, display screens of FPDs, and circuit boards for magnetic heads. A processing technique called photofabrication has become the mainstream of such precision processing technology. Photofabrication is a technique that involves: applying a photosensitive resin composition called photoresist to the surface of a workpiece to form a coating film (resist layer), followed by exposure; patterning the exposed coating film using a developer (forming a resist pattern); and performing electroforming (specifically, chemical etching, electrolytic etching, electroplating, or a combination thereof) by using the pattern as a mask, thereby forming various devices, wiring patterns and the like. This technique is used in the manufacturing of various precision components such as semiconductor packages.

[0003]

The developer used in photofabrication is an alkaline aqueous solution. However, metal ions contained in

alkaline aqueous solutions adversely affect the electrical properties of the resulting semiconductor packages and the like. To avoid this, metal-ion-free alkaline aqueous solutions, such as tetraalkylammonium hydroxide compound aqueous solutions (e.g., tetramethylammonium hydroxide (TMAH) aqueous solutions), are widely used as developers.

[0004]

Tetraalkylammonium hydroxide aqueous solutions are produced by electrolyzing tetraalkylammonium salts in an electrolytic cell using a cation exchange membrane as a diaphragm. Examples of the tetraalkylammonium salts for use in the production include chlorides, carboxylates, carbonates, and bicarbonates. When chlorides are used, they contaminate a target product at the cathode, namely, a tetraalkylammonium hydroxide aqueous solution. If such a tetraalkylammonium hydroxide aqueous solution is used for treatment of semiconductor substrates, their wiring could be corroded by chloride ions. It is thus important in producing tetraalkylammonium hydroxide aqueous solutions that the chloride ion concentration should be reduced to the mass ppb level. Chloride contamination is presumably due to traces of chloride ions inherent in the raw material passing through the cation exchange membrane, or trace components present in the raw material as impurities reacting or decomposing in the electrolytic cell to produce chloride ions.

[0005]

In order to reduce chloride ions, it has been proposed to heat components referred to as latent halides, which function as chloride ion precursors, present in tetraalkylammonium hydroxide aqueous solutions, at high temperature before electrolysis, thereby improving the purity of the solutions (see Patent Literature 1).

Prior Art Documents:

Patent Documents:

[0006]

Patent Literature 1: JP-B-2690730

Summary of the Invention:

Problems to be solved by the Invention:

[0007]

The method disclosed in Patent Literature 1 makes it possible to obtain a tetraalkylammonium hydroxide aqueous solution with a chloride ion content reduced to a few mass ppm. However, since the chloride ion concentration of this tetraalkylammonium hydroxide aqueous solution is not evaluated based on the mass ppb level, it is unknown whether the method of Patent Literature 1 enables production of a tetraalkylammonium hydroxide aqueous solution with a chloride ion content reduced to the mass ppb level. Further, the present inventors have found through their studies that high-temperature heating cannot always sufficiently reduce the chloride ion concentration.

[0008]

Further, the method of Patent Literature 1 includes subjecting a tetraalkylammonium hydroxide aqueous solution produced through electrolysis to high-temperature heating to decompose latent halides, followed by another electrolysis process to purify the solution. In other words, this method requires two electrolysis steps. Consequently, there have been demands for an industrially efficient production method for tetraalkylammonium hydroxide aqueous solutions.

Thus, an object of the present invention is to provide an industrially efficient method for producing a tetraalkylammonium hydroxide aqueous solution with a reduced chloride ion concentration.

Means for solving the Problems:

[0009]

To achieve the above-described object, the present inventors have made intensive studies and discovered the following: When tetraalkylammonium salts contain, as an impurity, a compound in which at least one hydrogen atom of the alkyl groups of the tetraalkylammonium salts is substituted with a chlorine atom (hereinafter, referred to as "halogenated tetraalkylammonium salt"), this impurity is so stable even when heated at 90°C that it cannot be removed sufficiently by such heating, and electrolysis of such tetraalkylammonium salts cannot produce a tetraalkylammonium hydroxide aqueous solution with a chloride ion content reduced to a desired level. The inventors have conducted further studies and found that electrolyzing tetraalkylammonium salts containing a predetermined amount of a halogenated tetraalkylammonium salt allows for industrially efficient production of a tetraalkylammonium hydroxide aqueous solution with a reduced chloride ion concentration, thereby completing the present invention.

[0010]

A first aspect of the present invention is a method for producing a tetraalkylammonium hydroxide aqueous solution through electrolysis of a tetraalkylammonium salt aqueous solution, wherein the tetraalkylammonium salt aqueous solution contains 500 mass ppb or less of a halogenated tetraalkylammonium salt relative to the tetraalkylammonium salt. In the first aspect of the present invention, the tetraalkylammonium salt aqueous solution preferably contains 100 to 500 mass ppb of the halogenated tetraalkylammonium salt relative to the tetraalkylammonium salt, and the tetraalkylammonium salt is preferably tetraalkylammonium chloride. Further, it is preferable to bring a tetraalkylammonium hydroxide-containing aqueous solution thus obtained into contact with

a cation exchange resin or a chelating resin.

[0011]

A second aspect of the present invention is a tetraalkylammonium hydroxide aqueous solution, including halogenated tetraalkylammonium ions at a concentration of 100 to 400 mass ppb relative to tetraalkylammonium ions. In the second aspect of the present invention, the tetraalkylammonium hydroxide aqueous solution preferably includes chloride ions at a concentration of 20 to 60 mass ppb relative to the tetraalkylammonium ions. Further, the tetraalkylammonium hydroxide aqueous solution preferably includes 5 mass ppt or less of each of the following metal impurities: Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb.

Effect of the Invention:

[0012]

The production method of the present invention uses as a raw material a tetraalkylammonium salt containing a predetermined amount of a halogenated tetraalkylammonium salt, thereby reducing the chloride ion concentration in the resultant tetraalkylammonium hydroxide aqueous solution. More specifically, the chloride ion concentration can be reduced to the order of mass ppb relative to tetraalkylammonium ions. Although details are unknown as to why the method of the present invention can reduce the chloride ion concentration in the tetraalkylammonium hydroxide aqueous solution, the present inventors presume as follows. That is, the halogenated tetraalkylammonium salt contained as an impurity in the tetraalkylammonium salt undergoes electrolytic reduction near the cathode and decomposes to produce chloride ions during electrolysis, resulting in an increased chloride ion concentration in the tetraalkylammonium hydroxide aqueous solution. It is considered that the halogenated

tetraalkylammonium salt is so stable even at high temperatures that it is hardly removed from the tetraalkylammonium salt sufficiently by a high-temperature treatment. Thus, using a tetraalkylammonium salt containing a predetermined amount of the halogenated tetraalkylammonium salt as a raw material presumably allows for a significant reduction in the chloride ion concentration in the tetraalkylammonium hydroxide aqueous solution.

Brief Description of the Drawings:

[0013]

[Figure 1]: Figure 1 is a schematic view illustrating the configuration of an electrolytic cell used in Examples of the present invention.

Mode for Carrying out the Invention:

[0014]

A production method of the present invention is characterized by the use of a tetraalkylammonium salt containing a predetermined amount of a halogenated tetraalkylammonium salt as a raw material. The method of the present invention will be described in detail below. Unless otherwise specified, numerical values represented herein as “A to B” refer to “A or more and B or less”. The unit attached only to value B also applies to value A.

[0015]

Tetraalkylammonium hydroxide aqueous solution

Examples of tetraalkylammonium hydroxide (hereinafter, also referred to as TAAH) include tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and trimethylethylammonium hydroxide. Among them, tetramethylammonium hydroxide is suitable due to its widespread use as a developer in a semiconductor

manufacturing process.

[0016]

The halide ion concentration in a tetraalkylammonium hydroxide aqueous solution can be analyzed by ion chromatography.

[0017]

Tetraalkylammonium salt aqueous solution

The TAAH aqueous solution containing the TAAH can be produced through electrolysis of a tetraalkylammonium salt aqueous solution having a desired tetraalkylammonium group, as described later. Specific examples of the tetraalkylammonium salt include halide salts, carbonates, carboxylates, and bicarbonates. Among them, halide salts and carbonates are suitable, and halide salts are particularly suitable, in view of easily obtaining a TAAH aqueous solution with a low metal impurity content. The halide may be appropriately selected from among chloride, bromide, and iodide.

[0018]

Halogenated tetraalkylammonium salt

According to the production method of the present invention, the content of the halogenated tetraalkylammonium salt relative to the tetraalkylammonium salt in the tetraalkylammonium salt aqueous solution is required to be 500 mass ppb or less. The halogenated tetraalkylammonium salt in the production method of the present invention refers to a compound in which at least one hydrogen atom of the four alkyl groups bonded to the nitrogen atom is halogenated. The halogen of the halogenated alkyl group is chlorine, bromine, or iodine. The number of the halogenated alkyl groups is not limited. For ease of purification, and considering that tetraalkylammonium salts are usually obtained through quaternization reaction of trialkylamines and alkyl halides, the number of the halogenated alkyl groups is

preferably one, in which case the halogenated tetraalkylammonium salt is a monohalogenated alkyl(trialkyl)ammonium salt. The carbon number of the halogenated alkyl group is not particularly limited either. For example, the halogenated alkyl group may have 1 to 10 carbon atoms, in which case the halogenated alkyl group is a halogenated methyl group, a halogenated ethyl group, a halogenated propyl group or the like.

[0019]

The content of the halogenated tetraalkylammonium salt relative to the tetraalkylammonium salt in the tetraalkylammonium salt aqueous solution may be appropriately determined within the range of 500 mass ppb or less depending on the TAAH aqueous solution to be obtained after electrolysis. In order to allow the TAAH aqueous solution to have a low chloride ion content, the content of the halogenated tetraalkylammonium salt is preferably 100 to 500 mass ppb.

[0020]

The halogenated tetraalkylammonium salt in the tetraalkylammonium salt aqueous solution can be analyzed by liquid chromatography-mass spectrometry (LC-MS) or ion chromatography.

[0021]

The halogenated tetraalkylammonium salt is relatively so heat-stable that it does not thermally decompose even when heated at 90°C. Thus, it is difficult to remove the halogenated tetraalkylammonium salt by heating. For removal of the halogenated tetraalkylammonium salt from the tetraalkylammonium salt, the tetraalkylammonium salt aqueous solution may be subjected, for example, to column chromatography using an ion exchange resin, or to an electric current in an electrolytic cell so that the halogenated tetraalkylammonium salt is electrolyzed.

[0022]

The presence of the halogenated tetraalkylammonium salt in the tetraalkylammonium salt is presumably due to impurities having two or more halogen elements present in alkyl halides as raw materials for the tetraalkylammonium salt. These impurities likely react with trialkylamine to undergo quaternization, thereby synthesizing halogenated tetraalkylammonium salts. For example, methyl chloride as a raw material for tetramethylammonium salts contains dichloromethane as an impurity at a level of several hundred volume ppm. If the dichloromethane in the methyl chloride can be reduced to nearly zero, (chloromethyl)trimethylammonium in the tetramethylammonium salts will also become nearly zero, and the chloride ion concentration relative to tetraalkylammonium ions is predicted to be 20 mass ppb or less.

[0023]

Electrolysis method

The production method of the present invention produces the TAAH aqueous solution through electrolysis of the tetraalkylammonium salt aqueous solution. Any known electrolysis method may be used without particular limitation. In general, an electrolytic cell is used that includes a cathode and an anode, between which only cation exchange membranes or both a cation exchange membrane and an anion exchange membrane are aligned, forming an intermediate compartment. The tetraalkylammonium salt aqueous solution is fed to this electrolytic cell, and acid is fed to an anode compartment on one side, whereby a tetraalkylammonium hydroxide aqueous solution is obtained in a cathode compartment on the other side.

[0024]

An acidic aqueous solution such as a hydrochloric acid solution is fed to the anode compartment. The tetraalkylammonium salt aqueous solution is fed to the intermediate compartment formed between the cation exchange

membrane and the anion exchange membrane. High-purity water, particularly ultrapure water or a high-purity tetraalkylammonium hydroxide aqueous solution, is fed to the cathode compartment.

[0025]

The cation exchange membrane and the anion exchange membrane used for the electrolysis are not particularly limited, and any known membrane conventionally used for the production of tetraalkylammonium hydroxide aqueous solutions through electrolysis may be used. Examples of the cation exchange membrane include membranes having sulfonic acid groups, carboxylic acid groups, or phosphoric acid groups. Examples of the anion exchange membrane include membranes to which one or more of the following are bonded: strongly basic ion exchange groups, such as quaternary ammonium bases, sulfonium bases, and phosphonium bases; and primary, secondary, and tertiary amines. Examples of a substrate for the ion exchange membranes include hydrocarbon-based resins, fluorocarbon resins, and perfluorocarbon resins. In particular, the substrate for the ion exchange membrane defining the cathode compartment is suitably a perfluorocarbon resin, which is stable under a basic atmosphere and has excellent durability. The substrate for the ion exchange membrane defining the anode compartment, where oxidizing gases such as halogen gas and oxygen gas are generated, is preferably a perfluorocarbon resin, which is resistant to oxidizing.

[0026]

The anode is suitably a so-called insoluble electrode whose titanium surface is coated with carbon, platinum-coated titanium, ruthenium, iridium or the like. The cathode is suitably made of a material that is stable in a strongly basic atmosphere and has a low overpotential, such as SUS316, platinum, and Raney nickel.

[0027]

In the electrolysis, the current density is appropriately 1 to 50 A/dm^2, and the temperature is controlled not to exceed 90°C, preferably at 30°C to 50°C.

[0028]

The production method of the present invention makes it possible to produce a tetraalkylammonium hydroxide aqueous solution with a low chloride ion concentration. More specifically, the concentration of halogenated tetraalkylammonium ions relative to tetraalkylammonium ions in the tetraalkylammonium hydroxide aqueous solution is 100 to 400 mass ppb, preferably 100 to 300 mass ppb, and particularly preferably 100 to 200 mass ppb.

[0029]

Removal of metal impurities

If metal impurities in the tetraalkylammonium hydroxide aqueous solution obtained by the production method of the present invention are a concern, they are removed from the tetraalkylammonium hydroxide aqueous solution, thereby obtaining a tetraalkylammonium hydroxide aqueous solution with a reduced metal impurity content. More specifically, the metal impurities may be removed by, for example, bringing the tetraalkylammonium hydroxide aqueous solution into contact with a cation exchange resin or a chelating resin so that the metal impurities are adsorbed to the cation exchange resin or the chelating resin.

[0030]

In the present invention, the metal impurities specifically refer to the following elements: Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb, and the metal impurity content refers to the total content of these elements. In the present invention, the metal impurity content in the tetraalkylammonium hydroxide aqueous solution is obtained through analysis with inductively coupled plasma mass

spectrometry (ICP-MS).

[0031]

Since the tetraalkylammonium hydroxide aqueous solution exhibits neutral to basic properties, the cation exchange resin may be either a strongly acidic cation exchange resin having sulfonic acid groups as cation exchange groups, or a weakly acidic cation exchange resin having carboxyl groups, phenolic hydroxyl groups or the like.

[0032]

Considering the possibility that the tetraalkylammonium hydroxide aqueous solution may exhibit acidity due to a trace amount of acid mixed therein during its production process, the cation exchange resin is preferably a strongly acidic cation exchange resin capable of ion exchange in a strongly acidic region. Alternatively, the tetraalkylammonium hydroxide aqueous solution may be brought into contact with a weakly acidic cation exchange resin after the acid is neutralized with a hydroxide having the same quaternary ammonium ions as those in the tetraalkylammonium hydroxide aqueous solution.

[0033]

The strongly acidic cation exchange resin usually has a structure in which a sulfonic acid group is introduced into a crosslinked resin matrix composed of a copolymer of a crosslinkable monomer and a monovinyl monomer as a cation exchange group-introducing precursor. Examples of the monovinyl monomer as a cation exchange group-introducing precursor include: styrene; alkyl-substituted styrenes such as methylstyrene and ethylstyrene; and halogen-substituted styrenes such as bromostyrene. These may be used alone or in combination of two or more. Above all, the monovinyl monomer is particularly preferably styrene or a styrene-based monomer.

[0034]

Examples of the crosslinkable monomer include monomers having multiple vinyl groups, such as divinylbenzene, trivinylbenzene, divinyltoluene, divinylnaphthalene, divinylxylene, divinylbiphenyl, bis(vinylphenyl)methane, bis(vinylphenyl)ethane, bis(vinylphenyl)propane, and bis(vinylphenyl)butane. These may be used alone or in combination of two or more. Above all, the crosslinkable monomer is particularly preferably divinylbenzene.

[0035]

The weakly acidic cation exchange resin may be a copolymer of a crosslinking monomer and a monovinyl monomer, such as acrylic acid and methacrylic acid, having the weakly acidic cation exchange group. The weakly acidic cation exchange resin is particularly preferably an acrylic acid-divinylbenzene copolymer or a methacrylic acid-divinylbenzene copolymer.

[0036]

The cation exchange resin may be of any type, such as a gel-type resin or a macroporous resin. Considering that a larger contact area between the ion exchange resin and the solution facilitates metal ion diffusion into the ion exchange resin, the cation exchange resin in the present invention is more suitably a macroporous resin.

[0037]

In addition, the cation exchange resin used in the present invention preferably has a cation exchange capacity in a range of 1.0 to 5.0 Eq/L, more preferably 1.5 to 3.0 Eq/L. The form of the cation exchange resin is not particularly limited, and the cation exchange resin may be in film form and is usually preferably in particle form.

[0038]

The chelating resin refers to a resin into which functional groups capable of forming complexes with metal ions are introduced. Due to its selective adsorptive

properties for specific metal ions, the chelating resin is applied to brine purification, plating solution purification, and removal of harmful metals. The chelating resin is also suitable for recovery of precious metals such as platinum and palladium.

[0039]

The functional group of the chelating resin usually contains two or more electron-donating elements, such as N, S, O, and P, and may be an N-O, S-N, N-N, O-O, P-N functional group or the like.

[0040]

Examples of the functional group of the chelating resin include iminodiacetic acid, polyamine, primary amine, methylglucamine, amidoxime, isothiouronium, thiol, sulfonic acid, phosphonic acid, aminophosphoric acid, bis-picolylamine, and semithiocarbamic acid. Among them, the functional group of the chelating resin is typically and preferably iminodiacetic acid or aminophosphoric acid due to its broad metal selectivity.

[0041]

The chelating resin may be of any type, such as a gel-type resin or a macroporous resin. Considering that a larger contact area between the chelating resin and the solution facilitates metal ion diffusion into the chelating resin, the chelating resin in the present invention is more suitably a macroporous resin.

[0042]

Counterions of the cation exchange resin or the chelating resin (hereinafter, also referred to collectively as “cation exchange resin, etc.”) may be either metal ions or non-metal ions. Specific examples of the non-metal counterions include hydrogen ions, ammonium ions (NH_4^+), and primary to quaternary ammonium ions.

[0043]

The counterions of the cation exchange resin, etc. in

the present invention are preferably non-metal ions, particularly hydrogen ions. When the counterions are ammonium ions (NH_4^+) or primary to quaternary ammonium ions, except in cases where the cations are the same quaternary ammonium ions as those in the tetraalkylammonium hydroxide aqueous solution, elution of different cations could cause contamination of the resulting tetraalkylammonium hydroxide aqueous solution with different ammonium compounds, in which case such contaminants are difficult to separate.

[0044]

When the counterions are hydrogen ions, in cases where the tetraalkylammonium hydroxide aqueous solution is a hydroxide solution, hydrogen ions released through exchange with metal ions are neutralized to form water, resulting in no contamination. In cases where the tetraalkylammonium hydroxide aqueous solution is not a hydroxide solution, a hydroxide having the same quaternary ammonium ions as those in the tetraalkylammonium hydroxide aqueous solution may be added, so that the acid derived from the released hydrogen ions is neutralized and converted into the tetraalkylammonium hydroxide aqueous solution and water, resulting in easy removal of contamination. Hydrogen ions may preferably constitute a part of the counterions, in which case the hydrogen ions preferably account for at least 1 mol%, more preferably at least 3 mol%, particularly preferably at least 10 mol%, and most preferably at least 20 mol%, of the counterions.

[0045]

In the present invention, the counterions of the cation exchange resin, etc. can be quantified for their components by ion chromatography, by bringing the cation exchange resin, etc. into contact with the acid to elute non-metal ions other than metal ions and hydrogen ions. For quantification of hydrogen ions, the cation exchange

resin, etc. is brought into contact with a salt to elute hydrogen ions, followed by neutralization titration.

[0046]

In cases where the cation exchange resin, etc. has metal counterions, or where the cation exchange resin, etc. having non-metal counterions contains a certain amount of metal ions that needs to be reduced in concentration, the cation exchange resin, etc. is brought into contact with an aqueous solution containing cations other than the metal ions so that the metal ions are removed, thereby obtaining the cation exchange resin, etc. having non-metal counterions. Considering that large-sized cations, such as tetraalkylammonium ions, are difficult to diffuse into the cation exchange resin, etc. if it is highly cross-linked as stated above, the aqueous solution to be brought into contact with the cation exchange resin, etc. preferably contains small-sized cations that can readily penetrate into the resin and be rapidly exchanged with the metal ions. More specifically, the aqueous solution is preferably an acidic solution containing hydrogen ions as the cations.

[0047]

Examples of the aqueous acidic solution to be brought into contact include inorganic acid aqueous solutions, such as sulfuric acid, hydrochloric acid, and nitric acid aqueous solutions. From the viewpoint of preventing resin material deterioration, hydrochloric acid and sulfuric acid aqueous solutions are preferred. Although there is no limitation on the acid concentration of the solution, contact with a highly concentrated acid causes rapid replacement of the counterions, which could result in cracking or damage of the resin due to sudden volume changes. To avoid this, the acid concentration is preferably 1 mol/L or less, more preferably 0.5 mol/L or less, and still more preferably 0.3 mol/L or less. It is

preferable to treat the cation exchange resin, etc. with an acid equivalent to 1.2 to 5 times, more preferably 1.5 to 3 times, the total exchange capacity of the cation exchange resin, etc.

[0048]

The aqueous acidic solution and the cation exchange resin, etc. may be brought into contact with each other by any process, such as batch or column process. In the case of column process using a resin column, it is preferable that the solution containing an acid equivalent to three times or more the exchange capacity of the cation exchange resin, etc. is passed through the resin column in either an upflow or downflow direction at any space velocity (SV), which is preferably in a range of 1 to 20 (1/hr) in view of treating time and efficiency. In the case of batch process, it is preferable that the solution containing an acid equivalent to 3 to 15 times the total exchange capacity of the cation exchange resin, etc. is replaced with a new solution three or more times.

[0049]

If the aqueous acidic solution has a high metal ion content, the metal ions may remain in the cation exchange resin, etc. depending on their concentration, which could result in decreased exchange capacity for metal ions and, in some cases, contamination with released metal ions during purification. To avoid this, the total content of metal impurities of Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb contained in the aqueous acidic solution is preferably 100 ppt or less, more preferably 10 ppt or less, and still more preferably 1 ppt or less.

[0050]

After being brought into contact with the aqueous acidic solution, the cation exchange resin, etc. is preferably washed with ultrapure water. This removes

excess acid adhering to the surface of the resin rather than serving as the counterion, thereby preventing acid contamination in subsequent processes. Since the tetraalkylammonium hydroxide aqueous solution is a hydroxide solution, residual acid on the cation exchange resin, etc. causes a neutralization reaction, followed by rapid heat generation, which could cause the resin to rupture due to rapid swelling. To avoid this, washing with ultrapure water is preferred.

[0051]

In bringing the cation exchange resin, etc. having hydrogen counterions into contact with the tetraalkylammonium hydroxide aqueous solution, the same acid concentration, contact process, and metal ion content as those described above for the contact with the aqueous acidic solution are suitably applied. Also, the cation exchange resin, etc. is preferably washed with ultrapure water after being brought into contact with the tetraalkylammonium hydroxide aqueous solution.

[0052]

In the present invention, the cation exchange resin, etc. may be brought into contact with the tetraalkylammonium hydroxide aqueous solution by any process, such as batch or column process, and industrially preferably by column process. Column process uses a resin column, through which the solution is passed for purification. The solution may be passed through the resin column in either an upflow or downflow direction, preferably in a downflow direction for improved purification efficiency. The space velocity (SV) is preferably 1 to 20 (1/hr), more preferably 5 to 20 (1/hr).

[0053]

The volume of the tetraalkylammonium hydroxide aqueous solution to be brought into contact is usually not less than 100 (L/L resin) for the sake of efficiency.

According to the method of the present invention, excellent metal ion removal efficiency is remarkably exhibited when a large volume of crude tetraalkylammonium hydroxide aqueous solution is treated, as stated above. In view of this, the volume of the crude tetraalkylammonium hydroxide aqueous solution relative to the volume of the cation exchange resin, etc. is effectively not less than 2000 (L/L resin), more preferably not less than 10000 (L/L resin). However, treating an excessively large volume of crude tetraalkylammonium hydroxide aqueous solution leads to reduced metal ion removal efficiency; thus, the volume is usually not more than 10^8 (L/L resin), particularly preferably not more than 50000 (L/L resin).

[0054]

It is efficient to subject the cation exchange resin, etc. with reduced metal ion removal efficiency to the acid treatment as a resin regeneration treatment, thereby enabling the solution to be repeatedly purified through this cation exchange resin, etc. The solution may be passed through two or more consecutive resin columns.

[0055]

Batch process purification involves immersion preferably in not less than 200 (L/L resin) of the tetraalkylammonium hydroxide aqueous solution from the viewpoint of remarkably exhibiting excellent metal ion removal efficiency. For a further reduction of the metal ions, it is preferred that batch process is performed repeatedly, preferably two to five times.

[0056]

In the present invention, in cases where the tetraalkylammonium hydroxide aqueous solution contains particulate metal impurities, it is preferable to remove these impurities through filtration before or after bringing the solution into contact with the cation exchange resin, etc. Particulate metal impurities or resin

particles contained in the crude tetraalkylammonium hydroxide aqueous solution could hinder the metal ion removal efficiency of the cation exchange resin, etc. in the present invention or cause clogging in column process. To avoid this, a filtration pretreatment is preferred. Alternatively, filtration may also be preferably performed as a post-treatment for fear that the solution may be contaminated after being brought into contact with the cation exchange resin, etc. with residual particulate metal impurities and, in some cases, with fragments of the cation exchange resin, etc.

[0057]

The average pore diameter of the filter is preferably 1 μm or less, more preferably 0.02 to 1 μm. If the average pore diameter of the filter is unknown, the pore diameter measured by the bubble point method is defined as the average pore diameter.

[0058]

It is desirable that the materials used for the inner walls of devices, such as containers, tanks, resin columns, and pipes, have chemical resistance and minimize metal contamination as much as possible. In this view, the materials are preferably polyethylene, polypropylene or fluorine-based resin, or lined with any of these resins. In particular, fluorine-based resin is most suitable from the perspective of preventing metal contamination. The surfaces of these members are preferably washed in advance before use with, for example, a tetraalkylammonium hydroxide aqueous solution or an acid.

[0059]

Tetraalkylammonium hydroxide aqueous solution

The above-described method enables effective production of a high-purity tetraalkylammonium hydroxide aqueous solution with reduced metal ions. More specifically, it is also possible to obtain a

tetraalkylammonium hydroxide aqueous solution having a total content of metal impurities of Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb of 100 ppt or less, more preferably 50 ppt or less, and still more preferably 20 ppt or less. Also, the content of each of these metal elements in the tetraalkylammonium hydroxide aqueous solution can be reduced to 30 ppt or less, more preferably 10 ppt or less, and still more preferably 5 ppt or less.

[0060]

Since the tetraalkylammonium hydroxide aqueous solution is strongly alkaline, some metal elements other than those described above may exist as anions or in non-ionic forms, in which case the removal efficiency may not be sufficiently exerted.

[0061]

The tetraalkylammonium hydroxide concentration in the tetraalkylammonium hydroxide aqueous solution may be appropriately set depending on the desired purpose. More specifically, the concentration may be appropriately set within a range of 0.5 to 40 mass%.

Examples:

[0062]

Hereinafter, the present invention will be described in more detail by way of Examples, but the present invention is not limited to these Examples. Examples 1 to 3 and Comparative Examples 1 to 3 used a three-compartment electrolyzer with an effective area of 1 dm^2 including an anion exchange membrane and a cation exchange membrane, as shown in Figure 1. An anode was made of a platinized titanium plate, and a cathode was made of SUS316.

[0063]

In the electrolyzer, 0.5 N sulfuric acid was added to an anode compartment; a 2.5 N tetramethylammonium chloride

aqueous solution as a test solution was added between the anion exchange membrane and the cation exchange membrane on the cathode side; and a quaternary ammonium hydroxide aqueous solution was added to a cathode compartment. These solutions were circulated while electrolysis was continuously performed at a current density of 30 A/dm^2 and a temperature of 40°C. During the continuous operation, the concentration of tetramethylammonium hydroxide in the cathode compartment was controlled at 2.0 N. Similarly, the concentration of the solution circulating through each of the compartments was kept constant by adding pure water when the solution had high concentration or adding the pertinent component when the solution had low concentration.

[0064]

After one month of continuous operation, the concentrations of (chloromethyl)trimethylammonium ions and chloride ions in the cathode compartment were confirmed in the following manner.

[0065]

(Chloromethyl)trimethylammonium ions were measured under the following LC-MS conditions, and their concentration was calculated using the peak area.

[0066]

LC-MS conditions

System: LCMS-2020, a liquid chromatograph mass spectrometer, manufactured by Shimadzu Corporation

Column: Atlantis HILIC Silica (manufactured by Nihon Waters K.K.), particle size: 3 μm, inner diameter: 2.1 mm, length: 150 mm

Column temperature: 40°C

Mobile phase: acetonitrile/50 mM ammonium formate aqueous solution containing 0.02% formic acid = 30/70 (V/V)

Flow rate: 0.2 mL/min

Ionization mode: ESI positive

Interface voltage: +4.5 kV

Measurement mode: SIM mode (m/z 118)

Nebulizer gas flow rate: 1.5 L/min

DL temperature: 250°C

Heat block temperature: 400°C

Drying gas flow rate: 15 L/min

Chloride ions were measured under the following ion chromatography conditions, and their concentration was calculated using the peak area.

[0067]

Ion chromatography conditions

System: Integrion manufactured by Thermo Fisher Scientific K.K.

Separation column: AS-18 IC Column (manufactured by Thermo Fisher Scientific K.K.), particle size: 7.5 μm, inner diameter: 2 mm, length: 250 mm

Column temperature: 35°C

Mobile phase: 20 mM potassium hydroxide aqueous solution

Detection method: conductivity

Sample loop: 100 μL

Sample conditions: 25% TMAH aqueous solution + ultrapure water (diluted 1:1)

[0068]

Example 1

A tetramethylammonium chloride aqueous solution, as a raw material, containing 221 mass ppb of (chloromethyl)trimethylammonium chloride relative to tetramethylammonium chloride was subjected to electrolysis, thereby producing a tetramethylammonium hydroxide aqueous solution. For the produced tetramethylammonium hydroxide aqueous solution, the concentration of (chloromethyl)trimethylammonium ions relative to tetramethylammonium ions was 246 mass ppb, and the concentration of chloride ions relative to

tetraalkylammonium ions was 25 mass ppb.

[0069]

Example 2

A tetramethylammonium chloride aqueous solution, as a raw material, containing 442 mass ppb of (chloromethyl)trimethylammonium chloride relative to tetramethylammonium chloride was subjected to electrolysis, thereby producing a tetramethylammonium hydroxide aqueous solution. For the produced tetramethylammonium hydroxide aqueous solution, the concentration of (chloromethyl)trimethylammonium ions relative to tetramethylammonium ions was 295 mass ppb, and the concentration of chloride ions relative to tetraalkylammonium ions was 59 mass ppb.

[0070]

Example 3

A tetramethylammonium chloride aqueous solution containing 660 mass ppb of (chloromethyl)trimethylammonium chloride relative to tetramethylammonium chloride was purified through electrolysis. A one-compartment electrolyzer (effective area: 1 dm^2) was prepared, which had the same structure and electrodes as those shown in Figure 1, except that the anion exchange membrane and the cation exchange membrane were removed. The tetramethylammonium chloride aqueous solution was added to the electrolyzer, to which a current with a current density of 30 A/dm^2 was applied for 10 consecutive hours at a temperature maintained at 40°C. As a result, the content of the (chloromethyl)trimethylammonium chloride relative to the tetramethylammonium chloride was reduced to 332 mass ppb. This tetramethylammonium chloride aqueous solution, as a raw material, was subjected to electrolysis, thereby producing a tetramethylammonium hydroxide aqueous solution. For the produced tetramethylammonium hydroxide aqueous solution, the concentration of

(chloromethyl)trimethylammonium ions relative to tetramethylammonium ions was 345 mass ppb, and the concentration of chloride ions relative to tetraalkylammonium ions was 39 mass ppb.

[0071]

Comparative Example 1

A tetramethylammonium chloride aqueous solution, as a raw material, containing 663 mass ppb of (chloromethyl)trimethylammonium chloride relative to tetramethylammonium chloride was subjected to electrolysis, thereby producing a tetramethylammonium hydroxide aqueous solution. For the produced tetramethylammonium hydroxide aqueous solution, the concentration of (chloromethyl)trimethylammonium ions relative to tetramethylammonium ions was 443 mass ppb, and the concentration of chloride ions relative to tetraalkylammonium ions was 98 mass ppb.

[0072]

Comparative Example 2

A tetramethylammonium chloride aqueous solution, as a raw material, containing 1769 mass ppb of (chloromethyl)trimethylammonium chloride relative to tetramethylammonium chloride was subjected to electrolysis, thereby producing a tetramethylammonium hydroxide aqueous solution. For the produced tetramethylammonium hydroxide aqueous solution, the concentration of (chloromethyl)trimethylammonium ions relative to tetramethylammonium ions was 1477 mass ppb, and the concentration of chloride ions relative to tetraalkylammonium ions was 246 mass ppb.

[0073]

Comparative Example 3

A tetramethylammonium chloride aqueous solution containing 660 mass ppb of (chloromethyl)trimethylammonium chloride relative to tetramethylammonium chloride was

heated at 90°C for five hours. As a result, the content of the (chloromethyl)trimethylammonium chloride relative to the tetramethylammonium chloride remained almost unchanged at 652 mass ppb. This tetramethylammonium chloride aqueous solution, as a raw material, was subjected to electrolysis, thereby producing a tetramethylammonium hydroxide aqueous solution. For the produced tetramethylammonium hydroxide aqueous solution, the concentration of (chloromethyl)trimethylammonium ions relative to tetramethylammonium ions was 492 mass ppb, and the concentration of chloride ions relative to tetraalkylammonium ions was 103 mass ppb.

[0074]

Table 1 shows the results of Examples 1 to 3 and Comparative Examples 1 to 3.

[0075]

[Table 1]

	Pretreatment for TMAC	CMTMAC/TMAC (mass ppb) in TMAC aqueous solution	$CMTMA^+/TMA^+$ (mass ppb) in TMAH aqueous solution	Cl^-/TMA^+ (mass ppb) in TMAH aqueous solution
Example 1	None	221	246	25
Example 2	None	442	295	59
Example 3	Purification	332	345	39
Comparative Example 1	None	663	443	98
Comparative Example 2	None	1769	1477	246
Comparative Example 3	Heating, 90ºC, 5 hrs	652	492	103

TMAC: tetramethylammonium chloride

CMTMAC: (chloromethyl)trimethylammonium chloride

TMAH: tetramethylammonium hydroxide

$CMTMA^+$: (chloromethyl)trimethylammonium ion

TMA^+: tetramethylammonium ion

Cl^-: chloride ion

[0076]

Example 4

The tetramethylammonium hydroxide aqueous solution with a chloride ion concentration of 25 mass ppb obtained in Example 1 was used as a crude tetramethylammonium hydroxide aqueous solution. For this crude tetramethylammonium hydroxide aqueous solution, the contents of metal impurities of Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb were measured. The measurements are shown in Table 2.

[0077]

Method of measuring metal impurity contents in tetraalkylammonium hydroxide aqueous solution

The concentrations of Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb were measured using a high-frequency inductively coupled plasma mass spectrometer (ICP-MS). The lower limit of measurement was 1 ppt, and values below 1 ppt were expressed as < 1 ppt.

[0078]

Next, a column (22 mm (ID) × 750 mm) was packed with 100 ml of an iminodiacetic acid-functionalized styrenic macroporous chelating resin (D5341 manufactured by Purolite; cation exchange capacity: 2.5 Eq/L). The packed column was subjected to the following pretreatment sequentially:

1) washing with ultrapure water;
2) treatment with 0.3 mol/L hydrochloric acid;
3) treatment with ultrapure water;
4) treatment with a 0.45 mol/L tetramethylammonium hydroxide aqueous solution; and
5) treatment with ultrapure water.

The volume of each of the solutions was 3 L, and the space velocity (SV) was 5 (1/hr).

[0079]

Each of the 0.3 mol/L hydrochloric acid and 0.45 mol/L tetramethylammonium hydroxide aqueous solutions

contained a total of 100 ppt or less of metal impurities of Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb. The ultrapure water contained a total of 1 ppt or less of metal impurities of Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb.

[0080]

2,000 L of the crude tetramethylammonium hydroxide aqueous solution was passed through the column at an SV of 20 (1/hr). When the loading volume reached 200 L (2,000 L/L resin), 500 L (5,000 L/L resin), 1,000 L (10,000 L/L resin), and 2,000 L (20,000 L/L resin), 1 L of the solution was collected for measurement of metal impurity contents. The measurements are shown in Table 2.

[0081]

[Table 2]

25% tetramethylammonium hydroxide aqueous solution	Metal impurity (ppt)						
	Li	Na	Mg	Al	K	Ca	Ti
Before purification	< 1	32	8	2	44	58	< 1
After purification (2,000 L/L resin)	< 1	1	< 1	2	< 1	2	< 1
After purification (5,000 L/L resin)	< 1	2	< 1	2	2	2	< 1
After purification (10,000 L/L resin)	< 1	< 1	< 1	2	1	1	< 1
After purification (20,000 L/L resin)	< 1	2	< 1	2	< 1	< 1	< 1

	Cr	Mn	Fe	Co	Ni	Cu	Zn
Before purification	< 1	< 1	1	< 1	6	< 1	213
After purification (2,000 L/L resin)	< 1	< 1	3	< 1	1	< 1	< 1
After purification (5,000 L/L resin)	1	< 1	2	< 1	2	< 1	< 1
After purification (10,000 L/L resin)	< 1	< 1	2	< 1	2	< 1	< 1
After purification (20,000 L/L resin)	< 1	< 1	2	< 1	1	< 1	< 1

	Ga	Mo	Ag	Cd	Sn	Ba	Pb
Before purification	< 1	< 1	< 1	< 1	< 1	46	10
After purification (2,000 L/L resin)	< 1	< 1	< 1	< 1	< 1	< 1	< 1
After purification (5,000 L/L resin)	< 1	< 1	< 1	< 1	< 1	< 1	< 1
After purification (10,000 L/L resin)	< 1	< 1	< 1	< 1	< 1	< 1	< 1
After purification (20,000 L/L resin)	< 1	< 1	< 1	< 1	< 1	< 1	< 1

[0082]

In Example 4, the tetramethylammonium hydroxide aqueous solution containing a total of 500 mass ppt or less of metal impurities of Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb was brought into contact with the chelating resin having non-metal counterion. As a result, the metal impurity concentration was reduced excellently when the loading volume reached 200 L (2,000 L/L resin), i.e., at an early stage after the start of the treatment, and this reducing effect lasted at least until the loading volume reached

2,000 L (20,000 L/L resin).

Explanations of Letters or Numerals:

[0083]

1: Anode

2: Cathode

3: Power source

4: Anode compartment

5: Raw material compartment

6: Cathode compartment

9: Proton permeation suppressing layer

10: Substrate layer

A: Anion exchange membrane

C1: Cation exchange membrane

CLAIMS

[Claim 1]

A method for producing a tetraalkylammonium hydroxide aqueous solution through electrolysis of a tetraalkylammonium salt aqueous solution, wherein

the tetraalkylammonium salt aqueous solution contains 500 mass ppb or less of a halogenated tetraalkylammonium salt relative to the tetraalkylammonium salt.

[Claim 2]

The method for producing a tetraalkylammonium hydroxide aqueous solution according to claim 1, wherein the tetraalkylammonium salt aqueous solution contains 100 to 500 mass ppb of the halogenated tetraalkylammonium salt relative to the tetraalkylammonium salt.

[Claim 3]

The method for producing a tetraalkylammonium hydroxide aqueous solution according to claim 1 or 2, wherein the tetraalkylammonium salt is tetraalkylammonium chloride.

[Claim 4]

A method for producing a tetraalkylammonium hydroxide aqueous solution, comprising: bringing a tetraalkylammonium hydroxide-containing aqueous solution obtained by the method of claim 1 into contact with a cation exchange resin or a chelating resin.

[Claim 5]

A tetraalkylammonium hydroxide aqueous solution, comprising halogenated tetraalkylammonium ions at a concentration of 100 to 400 mass ppb relative to tetraalkylammonium ions.

[Claim 6]

The tetraalkylammonium hydroxide aqueous solution according to claim 5, comprising chloride ions at a concentration of 20 to 60 mass ppb relative to the tetraalkylammonium ions.

[Claim 7]

The tetraalkylammonium hydroxide aqueous solution according to claim 5 or 6, comprising 5 mass ppt or less of each of the following metal impurities: Li, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Ba, and Pb.