

METHOD FOR THE TREATMENT OF TETRAALKYLAMMONIUM ION-
CONTAINING DEVELOPMENT WASTE LIQUOR

TECHNICAL FIELD

[0001]

The present invention relates to a treating method of tetraalkylammonium ion-containing development waste liquor. Particularly, the invention relates to a treating method of tetraalkylammonium ion-containing development waste liquor, in case of reusing cation exchange resin or chelate resin used for treatment of the development waste liquor, enabling to repeatedly recycle over a long period of time while inhibiting drastic swelling when converting a hydrogen ion form to a tetraalkylammonium ion form.

BACKGROUND ART

[0002]

Tetraalkylammonium hydroxide (hereinafter abbreviated to TAAH) is used as alkaline developer for photoresist in the photolithography process in the manufacturing process of electronic component such as semiconductor device, liquid-crystal display and printed-circuit board. Then, tetraalkylammonium ion (hereinafter abbreviated to TAA ion)-containing development waste

liquor, mainly comprising photoresist, including novolac resin as a main component, and TAA ion, is discharged in the developing step and washing step in the above photolithography process.

[0003]

In the past, the above TAA ion-containing development waste liquor has been rendered harmless by a publicly-known effluent treatment to dispose. Especially, recent increase in volume of manufacture of semiconductors and liquid crystals results in increased consumption of the developing solution, so that discharge of TAA ion-containing development waste liquor is also increased. Therefore, effective utilization of resources is studied, and there is proposed a method for reusing the TAA ion-containing development waste liquor, wherein TAAH is purified and reused by removing impurities such as photoresist-derived organic matter and metal ion from the above waste liquor. For example, there are proposed a method wherein the above development waste liquor is subject to electrodialysis or electrolysis to remove metal ions, etc., a method wherein metal ions, etc. in the above development waste liquor are removed by absorbing in cation exchange resin or chelate resin, or a method wherein metal ions, etc. in the above development waste liquor are

removed by absorbing in cation exchange resin or chelate resin, followed by electrolysis to purify and collect TAAH.

[0004]

Among these, as the method to remove metal ions, etc. in the above development waste liquor by absorbing in cation exchange resin or chelate resin, a method with the following steps is known: the cation exchange resin or chelate resin is converted into a hydrogen ion-form (H form) by acid, washed by ultrapure water, contacted with TAAH in a concentration of 1 mol/L to convert into a tetraalkylammonium ion-form (TAA ion form), and then contacted with the above TAA ion-containing development waste liquor to remove impurities such as metal ions. Further, there is proposed a reuse method of cation exchange resin or chelate resin in which the resin contacted with the development waste liquor is contacted with acid to remove metal ions, etc., and further converted into a TAA ion form for repeated use of the cation exchange resin or chelate resin (see Patent Document 1).

[0005]

However, the TAA ion form of the cation exchange resin or chelate resin is higher in water content than the H form, and swells. Consequently, when repeating the conversion between the H form and the TAA ion form, the

resin repeats contraction and swelling to cause a crack, so that the resin may fracture. Therefore, when the above resin is recycled for repeated use, the fractured resin may cause operational defects such as differential pressure when applying fluid, or remarkable reduction in flow rate.

[0006]

Also, Patent Document 2 discloses a treating method of a TAA ion-containing development waste liquor wherein a waste liquor with a TAA ion concentration of 0.016 mol/L or less (0.015 mass% or less) is used as the development waste liquor when an H form of a cation exchange resin or chelate resin is directly treated with a TAA ion-containing development waste liquor to absorb TAA ion into the resin, and followed by desorbing the TAA ion with acid, etc. The method is characterized in that drastic swelling of the above resin is inhibited by using a dilute TAA ion development waste liquor when converting into the TAA ion form. It is effective to inhibit deterioration of the cation exchange resin or chelate resin when recycling the above resin for repeated use. However, it is necessary to use a dilute solution as the development waste liquor, and there are problems in treatment efficiency such as increased waste liquor amount, etc. Also, the method has problems that it requires diluting operation such as adding

water when the development waste liquor to be treated is higher in concentration, causing the procedures more complex.

[0007]

[Patent Document 1] Japanese Unexamined Patent Publication No. 2003-190822

[Patent Document 2] Japanese Unexamined Patent Publication No. 2000-126766

DISCLOSURE OF INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0008]

Consequently, the purpose of the present invention is to provide a treating method of tetraalkylammonium ion-containing development waste liquor, industrially efficient without causing cracks to deteriorate early even when repeating reuse treatment of a cation exchange resin or chelate resin used for treatment of the development waste liquor.

MEANS FOR SOLVING THE PROBLEM

[0009]

The present inventors have been dedicated to studying for accomplishing the above purpose. First, the

present inventors studied a deterioration mechanism of a cation exchange resin or chelate resin when converting the resin from a H form into a TAA ion form. As a result, it was found that drastic swelling occurs due to heat of neutralization in addition to swelling caused by the TAA ion form when using a TAA ion solution with high TAA ion concentration, which accelerates the deterioration of the above resin. Based on the above findings, it was found that it is possible to simultaneously inhibit drastic swelling of the resin due to heat of neutralization and drastic swelling at conversion to the TAA ion form by combining an acid removal step, in which a H form of the cation exchange resin or chelate resin converted by contacting with acid is contacted with water until the pH of a solution eluted from the resin becomes 3 or more to remove acid, and a TAA ion-form conversion step, in which the resin is contacted with 0.3 to 0.8 mol/L of the TAA ion solution to convert into the TAA ion form, even when using relatively highly-concentrated TAA ion solution to convert into the TAA ion form, so that the present invention has been achieved.

[0010]

Namely, the present invention is a treating method of TAA ion-containing development waste liquor, comprising

(1) a H-form conversion step of bringing an acid into contact with a cation exchange resin or a chelate resin, (2) an acid removal step of bringing water into contact with the above resin after the H-form conversion step until pH of an eluate from the resin becomes 3 or more, (3) a TAA ion-form conversion step of bringing 0.3 mol/L to 0.8 mol/L of TAA ion solution into contact with the above resin after the acid removal step and (4) a development waste liquor treatment step of bringing a TAA ion-containing development waste liquor into contact with the cation exchange resin or chelate resin after the TAA ion-form conversion step to remove impurities in the waste liquor.

EFFECTS OF THE INVENTION

[0011]

According to the treating method of TAA ion-containing development waste liquor of the present invention, in case of converting the cation exchange resin or chelate resin used for the treatment from a H form to a TAA ion form, it is possible to simultaneously prevent drastic swellings of the resin due to heat of neutralization and conversion into the TAA ion form even when using relatively highly-concentrated TAA ion solution. Consequently, the resin can be repeatedly treated for

reuse without increase in waste liquor amount at the above conversion. Therefore, a stable and efficient refining treatment of TAA ion-containing development waste liquor is available.

BEST MODE FOR WORKING THE INVENTION

[0012]

A treating method of TAA ion-containing development waste liquor of the present invention comprises (1) a step for converting into H form (H-form conversion step) of bringing an acid into contact with a cation exchange resin or chelate resin, (2) an acid removal step of bringing water into contact with the above resin after the H-form conversion step until pH of an eluate from the resin becomes 3 or more, (3) a step for converting into TAA ion form (TAA ion-form conversion step) of bringing 0.3 mol/L to 0.8 mol/L of TAA ion solution into contact with the above resin after the acid removal step, and (4) a development waste liquor treatment step of bringing a TAA ion-containing development waste liquor into contact with the cation exchange resin or chelate resin after the TAA ion-form conversion step to remove impurities in the waste liquor.

[0013]

(Cation Exchange Resin or Chelate Resin)

As the cation exchange resin used in the treating method of TAA ion-containing development waste liquor of the present invention, for example, there may be mentioned a strongly acidic cation exchange resin in which a strongly acidic group such as sulfonic group is introduced into a base substance such as a styrene-divinylbenzene copolymer, an acrylic acid-divinylbenzene copolymer and a methacrylic acid-divinylbenzene copolymer, and a weakly acidic cation exchange resin in which a weakly acidic group such as carboxyl group and phenolic hydroxyl group is introduced into the above base substance. As a structure of the above resin, there are a gel form, a porous form, a high-porous form and a macroreticular (MR) form, and any of the above structures can preferably be used in the present invention. Particularly, the MR form, excellent in strength of swelling and contraction, is preferable.

[0014]

Also, as the chelate resin, for example, there may be mentioned resin in which a chelate-forming group is introduced in a styrene-divinylbenzene copolymer. The chelate-forming group includes an iminodiacetic acid form, an iminopropionic acid form, an amino phosphonic acid form such as an amino methylene phosphonic acid form, a

polyamine form, a glucamine form such as N-methylglucamine form, an aminocarboxylic acid form, a dithiocarbamic acid form, a pyridine form, a thiol form and an amidoxime form, etc.

[0015]

In the treating method of TAA ion-containing development waste liquor of the present invention, any of the above cation exchange resin or chelate resin can be used. In general, the cation exchange resin or chelate resin may be properly selected depending on a metal ion, etc. to be removed since removable metal ion, etc. varies depending on the kind of the resin. Also, each of the cation exchange resin or chelate resin may be used independently or plurally, and further, the cation exchange resin and chelate resin can be used in combination. As a method to use the above resin, either of a batch method or a column method is available. In the batch method, a solution for the above treatment is brought into contact with the cation exchange resin or chelate resin and stirred, followed by separating the cation exchange resin or chelate resin by filtration, etc.; and in the column method, a column is packed with the cation exchange resin or chelate resin, and then, a solution for the above treatment is circulated from the top or the bottom of the

column for bringing into contact with the cation exchange resin or chelate resin. Among these, it is preferable to use in the column method in the treating method of the present invention since it allows continuously performing each step.

[0016]

(H Form Conversion Step)

Normally, the above cation exchange resin or chelate resin is commercially available in a H form or sodium ion form (Na form). Since contamination of metal ions, etc. is strictly restricted in the semiconductor manufacturing process, etc., when using the above resin converted into TAA ion form to remove metal ions, etc. in the TAA ion-containing development waste liquor, the Na form of the resin is usually converted into the H form by contacting with an acid, followed by converting into the TAA ion form.

Also, when reusing the above resin after contacting with the TAA ion-containing development waste liquor, it is necessary to bring an acid into contact with the resin to remove impurities such as metal ions, and to convert the resin from the TAA ion form into the H form.

[0017]

Such an acid to contact with the cation exchange resin or chelate resin is not particularly limited as long

as the acid can produce a hydrogen ion in an aqueous solution. For example, a mineral acid aqueous solution such as hydrochloric acid and sulfuric acid may be illustrated. Among the above acids, because of its industrial availability at low price and ease of control of concentration, hydrochloric acid aqueous solution is most preferable. A concentration and amount of the above hydrochloric acid are not particularly limited as long as these are sufficient to convert into the H form and to remove impurities such as metal ions. Normally, it is enough to bring 1 to 10 mass% of hydrochloric acid aqueous solution in an amount of 3 to 10 (L/L-resin) into contact with the above cation exchange resin or chelate resin.

[0018]

In the above H-form conversion step, a contact method of the cation exchange resin or chelate resin with the acid is not particularly limited. To take the column method as an example, the acid may be supplied to the column packed with the cation exchange resin or chelate resin, either from the bottom of the column in upward flow, or from the top of the column in downward flow, and it is preferable to supply the acid in downward flow due to simple equipment configuration and little damage to the cation exchange resin or chelate resin. Also, smaller flow

rate of the acid in the column is better to reduce damage to the cation exchange resin or chelate resin, and space velocity (SV) is preferably 5 to 20 (1/hr) in terms of treating time and efficiency.

[0019]

(Acid Removal Step)

In the present invention, it is important for combination with the after-mentioned TAA ion-form conversion step to perform an acid removal step by bringing water into contact with the H-form converted cation exchange resin or chelate resin until pH of an eluate from the resin becomes 3 or more. Namely, by bringing water into contact with the above resin after the H-form conversion step until pH becomes 3 or more, it is possible to contact with relatively highly-concentrated TAA ion solution. When bringing the TAA ion solution into direct contact with the above resin containing residual acid to convert into the TAA ion form, neutralization proceeds rapidly to result in generating heat of neutralization, so that the above resin drastically swells. Therefore, by performing the acid removal step, it is possible to remove residual acid in the cation exchange resin or chelate resin, and to inhibit drastic swelling of the resin due to generation of the heat of neutralization when converting

into the TAA ion form.

[0020]

For inhibiting generation of the heat of neutralization at the successive conversion into the TAA ion form, it is sufficient to perform the acid removal step of the present invention until pH of the eluate from the above resin becomes 3 or more. However, from a viewpoint to inhibit damage to the above resin by removing the acid more securely, it is more preferable to perform the acid removal step until pH of the above eluate becomes 5 or more.

[0021]

Also, from a viewpoint that contamination of metal ions, etc. is strictly limited at treatment of the TAA ion-containing development waste liquor, the water used in the above acid removal step preferably has electric conductivity of 0.1 $\mu\text{S}/\text{cm}$ or less. As the water, ion-exchanged water and ultrapure water can be illustrated.

[0022]

A contact method of the cation exchange resin or chelate resin with the water in the above acid removal step is not particularly limited, and the same contact method as in the above H-form conversion step can be employed. For example, in the column method, a direction to contact with

water may be either upward or downward. Also, smaller flow rate of the water in the column is better to reduce damage to the cation exchange resin or chelate resin, and SV is preferably 5 to 20 (1/hr) in terms of treating time and efficiency.

[0023]

(TAA Ion Form Conversion Step)

In the treating method of TAA ion-containing development waste liquor of the present invention, it is important to perform the TAA ion-form conversion step by bringing TAA ion solution with a TAA ion concentration of 0.3 mol/L to 0.8 mol/L into contact with the above acid-removed cation exchange resin or chelate resin for converting into the TAA ion form. Namely, when the TAA ion concentration is lower than 0.3 mol/L, not only the amount of TAA ion solution required to convert the cation exchange resin or chelate resin into the TAA ion form, but also a waste liquor amount discharged in the above TAA ion-form conversion step may be increased, which is not preferable in terms of industrial efficiency. Also, when using the TAA ion solution in a concentration lower than 0.3 mol/L and decreasing its amount, the above resin may not sufficiently be converted into the TAA ion form, removal efficiency may be declined in absorbing and removing

impurities such as metal ions in the TAA ion-containing development waste liquor. On the other hand, when the TAA ion concentration exceeds 0.8 mol/L, it is impossible to inhibit drastic swelling of the above resin even with said acid removal step. Further, the above TAA ion concentration of the TAA ion solution is particularly preferably 0.3 mol/L to 0.5 mol/L from a viewpoint that working efficiency and inhibiting effect for drastic swelling of the resin are high.

[0024]

The TAA ion solution used in the present invention is not particularly limited as long as it is aqueous solution containing TAA ion, and for example, TAAH aqueous solution may be preferably used, which is a hydroxide of TAA ion such as a tetramethylammonium ion, a tetraethylammonium ion, a tetrapropylammonium ion and tetrabutylammonium ion. Further, when the cation exchange resin or chelate resin is a strongly acidic cation exchange resin, aqueous solution of TAA ion salt can preferably be used as the TAA ion solution, too. As a counterion of the TAA ion salt, for example, a chloride ion, a fluoride ion, a bromide ion, a carbonic acid ion, a bicarbonic acid ion, etc. may be mentioned. Among the above TAA ion solutions, the tetramethylammonium hydroxide aqueous solution and

aqueous solution of tetramethylammonium salt can particularly preferably be used since these are widely used as a developing solution in the semiconductor manufacturing process.

[0025]

Also, an amount of the TAA ion solution brought into contact with the cation exchange resin or chelate resin is not particularly limited as long as the amount is sufficient to convert the resin into the TAA ion form, and can properly be selected. In the above column method, 3 to 10 (L/L-resin) may be enough for contacting with the above resin.

[0026]

A contact method of the cation exchange resin or chelate resin with the TAA ion solution in the above TAA ion-form conversion step is not particularly limited, and the same contact method as in the above H-form conversion step can be employed. For example, in the column method, a direction to contact with the TAA ion solution may be either upward or downward. Also, smaller flow rate of the TAA ion solution in the column is better to reduce damage to the cation exchange resin or chelate resin, and SV is preferably 5 to 20 (1/hr) in terms of treating time and efficiency.

[0027]

(Development Waste Liquor Treatment Step)

In the treating method of TAA ion-containing development waste liquor of the present invention, the above TAA ion-form converted resin is then subject to a development waste liquor treatment step, wherein the TAA ion-containing development waste liquor is brought into contact with the resin to remove impurities such as metal ions in the waste liquor.

[0028]

As mentioned above, the TAA ion-containing development waste liquor mainly includes photoresist-derived organic matter, such as novolac resin, and TAAH. In general, the development waste liquor is alkaline showing pH of 12 to 14, and in the alkaline development waste liquor, the photoresist-derived organic matter is dissolved in salt form with the TAA ion via its acid group such as carboxyl group. Also, the above TAA ion-containing development waste liquor may be neutralized by an acid such as hydrochloric acid and carbonic acid gas for removing insolubilized photoresist-derived organic matter by filtration. In this case, the TAA ion in the above development waste liquor is present as a salt of other acid-derived anion. For example, when using carbonic acid

gas for neutralization, the TAA ion is present in the form of carbonate or bicarbonate.

[0029]

In the present invention, it is possible either to directly use the TAA ion-containing development waste liquor including the above photoresist-derived organic matter, or to use TAA ion-containing development waste liquor after neutralization by carbonic acid gas, etc. for removal of the photoresist-derived organic matter, without any particular limitation. However, it is preferable to use the TAA ion-containing development waste liquor after neutralization by carbonic acid gas, etc. for removal of the photoresist-derived organic matter in terms of inhibiting residual photoresist-derived organic matter in the above resin.

[0030]

In the development waste liquor treatment step of the present invention, TAA ion concentration and amount of the development waste liquor used for the treatment are not particularly limited, and it is possible to properly select in view of removal efficiency of impurities such as metal ions in the above resin, etc. For example, when using the development waste liquor with higher TAA ion concentration than the above TAA ion solution, it is possible to use the

cation exchange resin or chelate resin without causing crack and fracture.

[0031]

A contact method of the cation exchange resin or chelate resin with the development waste liquor in the above treatment is not particularly limited, the same contact method as in the above H-form conversion step can be employed. For example, in the column method, a direction to contact with the above TAA ion-containing development waste liquor may be either upward or downward. Also, as a flow rate of the above development waste liquor in the column, SV is preferably 5 to 20 (l/hr) in terms of treating time and efficiency.

[0032]

(Alkali-Washing Step)

There remain impurities such as metal ions in the above development waste liquor treated cation exchange resin or chelate resin. It is possible to remove the impurities from the resin via said H-form conversion step. However, there remain the photoresist-derived organic matters in addition to the impurities such as metal ions in the above resin, which may cause clogging and deterioration of the resin due to the organic matters precipitated by the acid. Therefore, it is preferable to perform an alkali-

washing step prior to the H-form conversion step. By the alkali-washing step, it is possible to dissolve and remove the photoresist-derived organic matters absorbed in the above resin.

[0033]

An alkali used in the alkali-washing step is not particularly limited as long as this allows dissolving the photoresist-derived organic matters, and it is possible to properly select an inorganic alkali such as sodium hydroxide and potassium hydroxide, an organic alkali such as TAAH, etc. Among these, TAAH is preferable in terms of removal efficiency of the photoresist-derived organic matter, inhibiting contamination of inorganic cation, etc. With too low concentration of the above alkali, a great amount of the alkali solution may be required when removing the photoresist-derived organic matters from the cation exchange resin or chelate resin, and the waste liquor amount may increase as well, which is not preferable in terms of industrial efficiency. Also, with too high concentration, drastic contraction and swelling of the above resin may easily occur via the alkali-washing step when using the development waste liquor in which the photoresist-derived organic matters are removed by neutralizing by the acid such as carbonic acid gas in

particular, causing deterioration of the resin. Therefore, alkali concentration is preferably 0.3 mol/L to 0.8 mol/L in the alkali-washing step. Amount of the alkali solution in the alkali-washing step is not particularly limited as long as it is sufficient to remove the photoresist-derived organic matters and can properly be selected.

[0034]

A contact method of the cation exchange resin or chelate resin with the alkali solution in the above alkali-washing step is not particularly limited, and the same contact method as in the above H-form conversion step can be employed. For example, in the column method, a direction to contact with the alkali solution may be either upward or downward. Also, as a flow rate of the alkali solution in the column, SV is preferably 5 to 20 (l/hr) in terms of treating time and efficiency.

[0035]

(Recycling Step)

In the treating method of TAA ion-containing development waste liquor of the present invention, it is possible to re-convert the above alkali-washed cation exchange resin or chelate resin into the TAA ion form by performing a recycling step to successively circulate the resin into said H-form conversion step. In the present

invention, drastic swelling of the above resin can particularly be inhibited in the TAA ion-form conversion step, and as a result, it is possible to inhibit generation of crack and fracture in the resin. Therefore, it is possible to repeatedly reuse the above resin, and to perform removal treatment of metal ions, etc. from the TAA ion-containing development waste liquor by the cation exchange resin or chelate resin, with industrial efficiency in terms of treating cost, etc.

EXAMPLE

[0036]

A method of the present invention will be explained further specifically based on the following examples, but the present invention is not limited to these examples.

[0037]

Development waste liquor (Sample 1) discharged from a liquid-crystal display factory, and development waste liquor (Sample 2) discharged from a semiconductor device factory were respectively concentrated by evaporation method, followed by neutralization by carbonic acid gas, and insolubilized photoresist-derived organic matter was filtered from the development waste liquors to prepare samples of TAA ion-containing development waste liquor.

Both of the above samples contained photoresist-derived organic matter and tetramethylammonium hydroxide (hereinafter abbreviated to TMAH), and had TAA ion concentration of 57 mass%. Water qualities of Samples 1 and 2 are shown in Table 1.

[0038]

[Table 1]

	Al (ppb)	Fe (ppb)	Na (ppb)	K (ppb)
Sample 1	332	63	149	190
Sample 2	542	77	378	114

[0039]

Note that the level of fracture of the cation exchange resin or chelate resin was obtained in the following Examples and Comparative Examples by taking supernatant fluid in the column right after the TAA ion-form conversion step and measuring absorbance at 500 nm by spectrophotometer after leaving undisturbed at room temperature for 1 minute. Therefore, the larger absorbance indicates samples harder to settle out, i.e. samples with more fractured resin.

[0040]

Also, removal performance of metal ion by using the reused chelate resin was evaluated as residual concentrations of Al ion and Fe ion in the sample after passing through the chelate resin; and removal performance

of metal ion by using the reused cation exchange resin was evaluated as residual concentrations of Na ion and K ion in the sample after passing through the cation exchange resin. The metal concentration was analyzed by high-frequency inductively coupled plasma mass spectrometry (ICP-MS).

[0041]

Example 1

100 mL of chelate resin having an amino phosphate group as a chelate forming group, Duolite C467 (product name of Rohm and Haas), was packed in a column. Then, the resin was converted into the TMA form by the following steps: ultrapure water washing, H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 5.7) and TAA ion form conversion step (0.5 mol/L of TMAH solution).

[0042]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin), and the space velocity of SV=5 (1/hr). Note that pH of an eluate after the acid removal step was 5.7.

[0043]

The above column, wherein the resin was converted into the TMA ion form, was applied with 8 L (80L/L-resin)

of Sample 1 at SV=20 (1/hr). Then, the chelate resin was treated for reuse in the following order: alkali-washing step (0.5 mol/L of TMAH solution), ultrapure water washing (ultrapure water at pH 5.7), H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 5.7) and TAA ion-form conversion step (0.5 mol/L of TMAH solution).

[0044]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin) and the space velocity of SV=5 (1/hr). Note that pH of eluate after each cycle of the acid removal step was 5.7. A cycle was defined as steps between applying Sample 1 to the column and reuse of the chelate resin, and total of 5 cycles were repeated.

[0045]

The level of fracture after 5 cycles was 0.007 Abs, and residual Al ion and Fe ion concentrations in Sample 1 after passing through the fifth cycle of chelate resin were respectively 5 ppb and 2 ppb. Further, when performing the sixth cycle, no reduction in the differential pressure and flow rate were shown, and the equivalent results were obtained as in the fifth cycle.

[0046]

Comparative Examples 1 and 2

Except for changing TMAH concentration at the TAA ion-form conversion step to 1 mol/L (Comparative Example 1) and 0.1 mol/L (Comparative Example 2), 5 cycles of applying Sample 1 to the column and reuse of the chelate resin were repeated by the same method as in Example 1.

[0047]

The levels of fracture after 5 cycles were 0.071 Abs (Comparative Example 1) and 0.001 Abs (Comparative Example 2), respectively. Residual Al ion concentrations in Sample 1 after passing through the fifth cycle of chelate resin were 4 ppb (Comparative Example 1) and 51 ppb (Comparative Example 2), respectively, and residual Fe ion concentration was 2 ppb in both Comparative Examples 1 and 2.

[0048]

As a result, it was found that heavy metal was removed but fracture of the resin due to repeated recycling steps when the concentration of the TAA ion solution was higher than 0.8 mol/L. Also, as a result of the sixth cycle after the above cycle, the differential pressure and flow rate were reduced due to fracture of the resin. Also, when the concentration of the TAA ion solution was lower than 0.3 mol/L, there was no fracture of the resin due to repeated recycling steps, but residual Al concentration was high in Sample 1, indicating low removal performance of

metal ion. This means the chelate resin was not completely reused. Namely, this suggests needs for increasing fluid amount of the TMAH solution when reusing.

[0049]

Comparative Example 3

Except for skipping the acid removal step after the H-form conversion step and directly performing the TAA ion-form conversion step, 5 cycles of applying Sample 1 to the column and reuse of the chelate resin were repeated by the same method as in Example 1. The level of fracture after 5 cycles was 0.029 Abs. Also, residual Al ion and Fe ion concentrations in Sample 1 after passing through the fifth cycle of chelate resin were 4 ppb and 2 ppb, respectively.

[0050]

As a result, when directly performing the TAA ion-form conversion step without the acid removal step, it was found that the fracture of the resin occurred due to the repeated recycling steps even in the concentration of the TAA ion solution of 0.3 mol/L to 0.8 mol/L. The results of the above Example 1 and Comparative Examples 1 to 3 are summarized in Table 2.

[0051]

[Table 2]

	Treated Sample	Packed resin	Acid Removal Step	TMAH solution (mol/L)	Fracture of resin (Abs)	Removal performance of metal ion (ppb)	
						Al	Fe
Example 1	Sample 1	A	Done	0.5	0.007	5	2
Comp. Example 1	Sample 1	A	Done	1	0.071	4	2
Comp. Example 2	Sample 1	A	Done	0.1	0.001	51	2
Comp. Example 3	Sample 1	A	No	0.5	0.029	4	2

* Kind of packed resin

A: chelate resin Duolite C467

[0052]

Examples 2 and 3

Except for changing TMAH concentrations at the TAA ion-form conversion step to 0.3 mol/L (Example 2) and 0.7 mol/L (Example 3), 5 cycles of applying Sample 1 to the column and reuse of the chelate resin were repeated by the same method as in Example 1. The levels of fracture after 5 cycles were 0.004 Abs in Example 2 and 0.010 Abs in Example 3. Also, residual Al ion concentrations in Sample 1 after passing through the fifth cycle of chelate resin were 5 ppb (Example 2) and 4 ppb (Example 3), respectively; and residual Fe ion concentrations were 2 ppb (Example 2) and 2 ppb (Example 3), respectively.

[0053]

Example 4

Except for changing the sample to be treated by the chelate resin from Sample 1 to Sample 2, 5 cycles of applying Sample 2 to the column and reuse of the chelate resin were repeated by the same method as in Example 1. The level of fracture after 5 cycles was 0.007 Abs, and residual Al ion and Fe ion concentrations in Sample 2 after passing through the fifth cycle of chelate resin were 5 ppb and 4 ppb, respectively.

[0054]

Example 5

Except for changing the chelate resin to chelate resin having an amino phosphate group as a chelate forming group, Lewatit TP260 (product name of Bayer Corporation), 5 cycles of applying Sample 1 to the column and reuse of the chelate resin were repeated by the same method as in Example 1. The level of fracture after 5 cycles was 0.005 Abs, and residual Al ion and Fe ion concentrations in Sample 1 after passing through the fifth cycle of chelate resin were 4 ppb and 2 ppb, respectively.

[0055]

The results of the above Examples 2 to 5 are summarized in Table 3.

[0056]

[Table 3]

	Treated Sample	Packed resin	Acid Removal Step	TMAH solution (mol/L)	Fracture of resin (Abs)	Removal performance of metal ion (ppb)	
						Al	Fe
Example 2	Sample 1	A	Done	0.3	0.004	5	2
Example 3	Sample 1	A	Done	0.7	0.01	4	2
Example 4	Sample 2	A	Done	0.5	0.007	5	4
Example 5	Sample 1	B	Done	0.3	0.005	4	2

* Kind of packed resin

A: chelate resin Duolite C467

B: chelate resin Lewatit TP260

[0057]

Example 6

50 mL of strongly acidic cation exchange resin, Amberlyst 15 WET (product name of Rohm and Haas), was packed in a column. Next, the resin was converted into the TMA form by the following steps: ultrapure water washing, H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 5.7) and TAA ion-form conversion step (0.5 mol/L of TMAH solution).

[0058]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin) and the space velocity of SV=5 (1/hr). Note that pH of eluate after the acid removal step was 5.7.

[0059]

The above column, wherein the resin was converted into the TMA ion form, was applied with 10 L (200L/L-resin) of Sample 1 at SV=20 (1/hr). Then, the strongly acidic cation exchange resin was treated for reuse in the following order: alkali-washing step (0.5 mol/L of TMAH solution), ultrapure water washing (ultrapure water at pH 5.7), H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 5.7) and TAA ion-form conversion step (0.5 mol/L of TMAH solution).

[0060]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin) and the space velocity of SV=5 (1/hr). Note that pH of eluate after each cycle of the acid removal step was 5.7. A cycle was defined as steps between applying Sample 1 to the column and reuse of the cation exchange resin, and total of 5 cycles were repeated.

[0061]

The level of fracture after 5 cycles was 0.002 Abs, and residual Na ion and K ion concentrations in Sample 1 after passing through the fifth cycle of cation exchange resin were both less than 1 ppb. Further, when performing the sixth cycle, no reduction in the differential pressure and flow rate were shown, and the equivalent results were obtained as in the fifth cycle. It was found that there

was no fracture of the resin due to repeated recycling steps, and that Na ion and K ion in Sample 1 after passing through the cation exchange resin were removed.

[0062]

Comparative Examples 4 and 5

Except for changing the TMAH concentrations at the TAA ion-form conversion step to 0.1 mol/L (Comparative Example 4) and 1 mol/L (Comparative Example 5), 5 cycles of applying Sample 1 to the column and reuse of the strongly acidic cation exchange resin were repeated by the same method as in Example 6. The levels of fracture after 5 cycles were 0.002 Abs (Comparative Example 4) and 0.011 Abs (Comparative Example 5), respectively. Residual Na ion concentrations in Sample 1 after passing through the fifth cycle of cation exchange resin were 97 ppb (Comparative Example 4) and <1 ppb (Comparative Example 5), respectively, and residual K ion concentrations were 58 ppb (Comparative Example 4) and <1 ppb (Comparative Example 5), respectively.

[0063]

As a result, it was found in case of using the cation exchange resin that when concentration of the TAA ion solution was lower than 0.3 mol/L, there was no fracture of the resin due to the repeated recycling steps,

but that removal performance of Na ion and K ion of the cation exchange resin was low and the reuse was incomplete.

It was also found that when the concentration was higher than 0.8 mol/L, Na and K removal performance of the cation exchange resin was not lowered, but that fracture of the resin occurred due to the repeated recycling steps. Also, when performing the sixth cycle after the above cycles, the differential pressure and flow rate were reduced.

[0064]

The results of the above Example 6 and Comparative Examples 4 and 5 are summarized in Table 4.

[0065]

[Table 4]

	Treated Sample	Packed resin	Acid Removal Step	TMAH solution (mol/L)	Fracture of resin (Abs)	Removal performance of metal ion (ppb)	
						Na	K
Example 6	Sample 1	C	Done	0.5	0.002	<1	<1
Comp. Example 4	Sample 1	C	Done	0.1	0.002	97	58
Comp. Example 5	Sample 1	C	Done	1	0.011	<1	<1

* Kind of packed resin

C: strongly acidic cation exchange resin Amberlyst 15WET

[0066]

Example 7

10 L of chelate resin having an amino phosphate group as a chelate-forming group, Duolite C467 (product name of Rohm and Haas), was packed in a Column 1 with a diameter of 150 mm and a height of 2000 mm made of transparent vinyl chloride. The resin of this Column 1 was converted into the TMA form by the following procedure: ultrapure water washing, H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 6.9) and TAA ion-form conversion step (0.5 mol/L of TMAH solution).

[0067]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin), and the space velocity of SV=5 (1/hr). Note that pH of eluate after the acid removal step was 3.5.

[0068]

The above Column 1, wherein the resin was converted into the TMA ion form, was applied with 800 L (80L/L-resin) of Sample 1 at SV=10 (1/hr). Then, the chelate resin was treated for reuse in the following order: alkali-washing step (0.5 mol/L of TMAH solution), ultrapure water washing (ultrapure water at pH 6.9), H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 6.9) and TAA ion-form conversion step (0.5 mol/L of

TMAH solution).

[0069]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin), and the space velocity of SV=5 (1/hr). Note that pH of eluate after each cycle of the acid removal step was 3.5. A cycle was defined as steps between applying Sample 1 to the column and reuse of the chelate resin, and total of 8 cycles were repeated. The eluate after passing through Column 1 of Sample 1 was received in a Receiver Tank 1.

[0070]

The level of fracture after 1 cycle was 0.002 Abs, and residual Al ion and Fe ion concentrations in Sample 1 after passing through the first cycle of chelate resin were respectively 2 ppb and 2 ppb. On the other hand, the level of fracture after 8 cycles was 0.007 Abs, and residual Al ion and Fe ion concentrations in Sample 1 after passing through the eighth cycle of chelate resin were respectively 3 ppb and 2 ppb. Further, when performing the ninth cycle, no reduction in the differential pressure and flow rate were shown, and the equivalent results were obtained as in the eighth cycle.

[0071]

Next, 10L of strongly acidic cation exchange resin,

Amberlyst 15WET (product name of Rohm and Haas), was packed in a Column 2 with a diameter of 150 mm and a height of 2000 mm made of transparent vinyl chloride. The resin of this Column 2 was converted into the TMA form by the following procedure: ultrapure water washing, H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 6.9) and TAA ion-form conversion step (0.5 mol/L of TMAH solution).

[0072]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin), and the space velocity of SV=5 (1/hr). Note that pH of eluate after the acid removal step was 3.5.

[0073]

The above Column 2, wherein the resin was converted into the TMA ion form, was applied with 400 L (40L/L-resin) of the eluate in the Receiver Tank 1, obtained by passing Sample 1 through Column 1, at SV=20 (1/hr). Then, the strongly acidic cation exchange resin was treated for reuse in the following order: alkali-washing step (0.5 mol/L of TMAH solution), ultrapure water washing (ultrapure water at pH 6.9), H-form conversion step (1 mol/L of HCl solution), acid removal step (ultrapure water at pH 6.9) and TAA ion-form conversion step (0.5 mol/L of TMAH solution).

[0074]

Fluid was applied in each step so as to have a fluid amount of 5 (L/L-resin), and the space velocity of SV=5 (1/hr). Note that pH of eluate after each cycle of the acid removal step was 3.5.

[0075]

A cycle was defined as steps between applying the eluate in the Receiver Tank 1 obtained by passing Sample 1 through Column 1 and reuse of the cation exchange resin, and total of 8 cycles were repeated. The eluate after passing Sample 1 in the Receiver Tank 1, obtained by passing through Column 1, through the Column 2 was received in a Receiver Tank 2.

[0076]

The level of fracture after 1 cycle was 0.001 Abs, and residual Na ion and K ion concentrations in the eluate obtained after passing through the first cycle of chelate resin were both < 1 ppb. On the other hand, the level of fracture after 8 cycles was 0.002 Abs, and residual Na ion and K ion concentrations in the eluate after passing through the eighth cycle of chelate resin were both < 1 ppb. Further, when performing the ninth cycle, no reduction in the differential pressure and flow rate were shown, and the equivalent results were obtained as in the

eighth cycle. It was found that there was no fracture of the resin due to the repeated recycling steps, and that Na ion and K ion in the eluate after passing through the cation exchange resin were removed.

[0077]

The results of the above Example 7 are summarized in Table 5.

[0078]

[Table 5]

		Column 1			Column 2		
Kind of packed resin		A			C		
		Fracture of resin (Abs)	Removal performance of metal ion (ppb)		Fracture of resin (Abs)	Removal performance of metal ion (ppb)	
			Al	Fe		Na	K
No. of cycles	1	0.002	2	2	0.001	<1	<1
	8	0.007	3	2	0.002	<1	<1

* fluid amount in the TAA ion-form conversion step: 0.5 mol/L both in Column 1 and Column 2

* treated sample: Sample 1

* Kind of packed resin

A: chelate resin Duolite C467

C: strongly acidic cation exchange resin Amberlyst 15 WET

[0079]

Reference Example

5 mL of chelate resin having an amino phosphate group as a chelate-forming group, Duolite C467 (product name of Rohm and Haas), was packed in a column. Then, the resin was subject to the following steps: ultrapure water washing, H-form conversion step (1 mol/L of HCl solution) and acid removal step (ultrapure water at pH 6.9). The fluid was applied so that the fluid amounts were 5 (L/L-resin) in the ultrapure water washing and H-form conversion step, and 10 (L/L-resin) in the acid removal step, and that the space velocity was $SV=5$ (1/hr). Then, 5 mL of the eluate of the acid removal step was sampled at the lower exit of the column to measure the pH. The results are shown in Table 6.

[Table 6]

Fluid Amount (L/L-resin)	pH
1	1.30
2	1.32
3	1.52
4	2.28
5	3.50
6	4.60
7	5.23
8	5.29
9	5.45
10	5.70

[0080]

It was confirmed that pH became 3 or more when flowing 5L/L-resin or more of ultrapure water at pH 6.9 in the acid removal step.

CLAIMS

1. A treating method of tetraalkylammonium ion-containing development waste liquor comprising the following steps:

(1) a hydrogen ion-form conversion step of bringing an acid into contact with a cation exchange resin or a chelate resin to convert the resin into a hydrogen ion-form,

(2) an acid removal step of bringing water into contact with the cation exchange resin or chelate resin after the hydrogen ion-form conversion step until pH of an eluate from the resin becomes 3 or more,

(3) a tetraalkylammonium ion-form conversion step of bringing 0.3 mol/L to 0.8 mol/L of tetraalkylammonium ion solution into contact with the cation exchange resin or chelate resin after the acid removal step, and

(4) a development waste liquor treatment step of bringing a tetraalkylammonium ion-containing development waste liquor into contact with the cation exchange resin or the chelate resin after the tetraalkylammonium ion-form conversion step to remove impurities in the waste liquor.

2. The treating method of tetraalkylammonium ion-

containing development waste liquor as set forth in claim 1, comprising a recycling step of recycling the cation exchange resin or chelate resin after said development waste liquor treatment step in said hydrogen ion-form conversion step.

3. The treating method of tetraalkylammonium ion-containing development waste liquor as set forth in claim 2, comprising an alkali-washing step of bringing an alkali into contact with the cation exchange resin or chelate resin prior to said recycling step.