For removal of a metal ion from a quaternary ammonium compound aqueous solution, adsorption treatment with a cation-exchange resin is considered effective. For example, Patent Document 1 shows that such treatment is applied to a quaternary ammonium hydroxide compound aqueous solution synthesized by the electrolysis method described above, and the concentrations of metal ions, such as a Na ion and a Ca ion, are each decreased to 1 ppb or less (see [0016] Reference Example 1 and the like).

[0006]

In addition, it is also known that adsorption treatment of a crude quaternary ammonium hydroxide compound aqueous solution (in the present invention, the crude quaternary ammonium hydroxide compound aqueous solution is a quaternary ammonium hydroxide compound aqueous solution containing 1000 ppm or less of an organic impurity with a molecular weight of 1000 g/mol or more and containing a metal impurity) with a cation-exchange resin is also applied for the purpose of recovering the quaternary ammonium hydroxide compound component from a waste liquid when the quaternary ammonium hydroxide compound aqueous solution is used in a photoresist developer for manufacturing a semiconductor (e.g., Patent Document 2). Here, with reference to Patent Document 3 (lower right column in page 3), a strongly acidic cation-exchange resin product shown as a representative example of the cation-exchange resin and used in Example 1 in Patent Document 2 is described as a resin with a degree of cross-linking of 2 to 10%.

Prior Art Documents

Patent Document

[0007]

Patent Document 1: JP H06-025880 A

Patent Document 2: JP 2003-190949 A

Patent Document 3: JP H01-098617 A

Summary of Invention

Technical Problem

[0008]

Also in the adsorption treatment for the photoresist developer waste liquid with a cation-exchange resin, the effect of decreasing a metal ion has not been sufficiently satisfactory in many cases, either. Furthermore, a study by the present inventors have observed a phenomenon in which even though the effect of decreasing a metal ion is exhibited to a certain high degree at the initial stage of the treatment by selecting the cation-exchange resin in this case, the decreasing effect rapidly deteriorates when the purification is continued and the treatment amount increases. For this reason, the knowledge of removing a metal ion in the case where a developer waste liquid is a liquid to be treated has not been able to be taken into consideration for the purification of the quaternary ammonium compound aqueous solution prepared by the synthesis described

column and passing the solution. The liquid flow direction can be either upward flow or downward flow and is preferably downward flow from the viewpoint of increasing purification efficiency. The liquid flow condition is preferably a condition of a space velocity SV = 1 to 20 (1/hr), more preferably a condition of 5 to 20 (1/hr), and even more preferably a condition of 8 to 20 (1/hr).

[0053]

For the treatment amount of the crude quaternary ammonium compound aqueous solution to be brought into contact, usually 100 (L/L-resin) or more is efficient. As described above, the excellent effect of removing the metal ion in the method of the present invention is significantly exhibited when the treatment amount of the crude quaternary ammonium compound aqueous solution amounts to a large quantity. Thus, the treatment amount achieving a condition where the crude quaternary ammonium compound aqueous solution to the cation-exchange resin is 2000 (L/L-resin) or more and more preferably 10000 (L/L-resin) or more is more effective. However, if the treatment amount increases too much, the effect of removing the metal ion is reduced. Thus, the treatment amount is usually 10^8 (L/L-resin) or less and particularly preferably 50000 (L/L-resin) or less.

[0054]

For the cation-exchange resin whose effect of removing the metal ion has been thus reduced, it is efficient to subject such a cation-exchange resin to the acid treatment as a resin regeneration treatment, then resume the liquid flow, and repeat purification. In addition, the solution can be passed through two or more resin columns in series.

[0055]

On the other hand, in the purification by a batch method, the crude quaternary ammonium compound aqueous solution is preferably immersed in an amount of 200 L/L-resin or more from the viewpoint of significantly exhibiting the excellent effect of removing the metal ion. In addition, repeating the batch treatment can further decrease the metal ion, which is thus preferred. The number of repetitions is favorably two to five times.

[0056]

In the method of the present invention, when a particulate metal impurity is contained in the crude quaternary ammonium compound aqueous solution, the solution is preferably subjected to filter treatment as a step before or after the contact with the cation-exchange resin to remove the impurity. If a particulate metal impurity or a resin particle is contained in the crude quaternary ammonium compound aqueous solution, this may interfere with the action in the removal of the metal ion by the cation-exchange resin in the present invention or may cause clogging in the case of a liquid flow method. Thus, the solution is preferably subjected to filter treatment as a pretreatment. In addition, in the filter treatment, a particulate metal impurity remaining after contact with the cation-exchange resin and, in some cases, a broken piece of the cation-exchange resin may mix in. Thus, the filter treatment is also preferably performed as a post-treatment.

[0057]

packed in a column with a diameter of 22 mm x 750 mm. As a pretreatment, liquids were passed through this packed column in the following order:

1) ultrapure water washing,

2) 0.3 mol/L hydrochloric acid treatment,

3) ultrapure water treatment,

4) 0.3 mol/L ethyltrimethylammonium hydroxide aqueous solution treatment, and

5) ultrapure water treatment. The liquid flow amount of each liquid was 600 mL, and the space velocity was adjusted to SV = 5 (1/hr).

[0070]

Each of the 0.3 mol/L hydrochloric acid and the 0.3 mol/L ethyltrimethylammonium hydroxide aqueous solution had properties of a total content of the metal impurities composed of Na, K, Li, Ca, Mg, and Sr of 100 ppt or less and a total content of the metal impurities composed of Fe, Ni, Cu, and Pb of also 100 ppt or less. In addition, for the ultrapure water, a liquid with a total content of the metal impurities composed of Na, K, Li, Ca, Mg, Sr, Fe, Ni, Cu, and Pb of 1 ppt or less was used. Furthermore, the proportions of quaternary ammonium ions and hydrogen ions contained in the counter ions of the strongly acidic ion-exchange resin after the pretreatment were measured to find that the proportion of quaternary ammonium ions was 77 mol% and the proportion of hydrogen ions was 23 mol%.

[0071]

Through the column, 1050 L of a crude ethyltrimethylammonium chloride aqueous solution was passed under a condition of SV = 20 (1/hr). Each time after the liquid flow amount reached 10 L (200 L/L-resin), 100 L (2000 L/L-resin), 500 L (10000 L/L-resin), and 1000 L (20000 L/L-resin), 10 L of the corresponding liquid was collected, and the contents of the metal impurities were measured. The results are each shown in Tables 1 and 2.

[0072]

Example 2

The same operation as in Example 1 was performed except for changing the strongly acidic ion-exchange resin to be used to Diaion UBK16 (degree of cross-linking 16, cation exchange capacity 2.3 equiv/L, Mitsubishi Chemical Corporation) in Example 1. The proportion of quaternary ammonium ions contained in the counter ions of the strongly acidic ion-exchange resin after the pretreatment at this time was 87 mol%, and the proportion of hydrogen ions was 13 mol%. The measurement results of the metal impurity contents are each shown in Tables 1 and 2 above.

[0073]

Example 3

The same operation as in Example 1 was performed except for changing the strongly acidic ion-exchange resin to be used to Diaion SK112 (degree of cross-linking 12, cation exchange capacity 2.1 equiv/L, available from Mitsubishi Chemical Corporation) in Example 1. The proportion of quaternary ammonium ions contained in the counter ions of the strongly acidic

4) 0.3 mol/L tetramethylammonium hydroxide aqueous solution treatment, and

5) ultrapure water treatment. The liquid flow amount of each liquid was 600 mL, and the space velocity was adjusted to SV = 5 (1/hr).

[0088]

Each of the 0.3 mol/L hydrochloric acid and the 0.3 mol/L tetramethylammonium hydroxide aqueous solution had properties of a total content of the metal impurities composed of Na, K, Li, Ca, Mg, and Sr of 100 ppt or less and a total content of the metal impurities composed of Fe, Ni, Cu, and Pb of also 100 ppt or less. In addition, for the ultrapure water, a liquid with a total content of the metal impurities composed of Na, K, Li, Ca, Mg, Sr, Fe, Ni, Cu, and Pb of 1 ppt or less was used. Furthermore, the proportions of quaternary ammonium ions and hydrogen ions contained in the counter ions of the strongly acidic ion-exchange resin after the pretreatment were measured to find that the proportion of quaternary ammonium ions was 80 mol% and the proportion of hydrogen ions was 20 mol%.

[0089]

Through the column, 1050 L of the crude tetramethylammonium chloride aqueous solution was passed under a condition of SV = 20 (1/hr). Each time after the liquid flow amount reached 10 L (200 L/L-resin), 100 L (2000 L/L-resin), 500 L (10000 L/L-resin), and 1000 L (20000 L/L-resin), 10 L of the corresponding liquid was collected, and the contents of the metal impurities were measured. The results are each shown in Tables 7 and 8.

[0090]

Comparative Example 3

The same operation as in Comparative Example 2 was performed except for changing the strongly acidic ion-exchange resin to be used to Diaion UBK16 (degree of cross-linking 16, cation exchange capacity 2.3 equiv/L, Mitsubishi Chemical Corporation) in Comparative Example 2. The proportion of quaternary ammonium ions contained in the counter ions of the strongly acidic ion-exchange resin after the pretreatment at this time was 89 mol%, and the proportion of hydrogen ions was 11 mol%. The measurement results of the metal impurity contents are each shown in Tables 7 and 8.

[0091]

Comparative Example 4

The same operation as in Example 1 was performed except for changing the strongly acidic ion-exchange resin to be used to Diaion SK112 (degree of cross-linking 12, cation exchange capacity 2.1 equiv/L, available from Mitsubishi Chemical Corporation) in comparative Example 2. The proportion of quaternary ammonium ions contained in the counter ions of the strongly acidic ion-exchange resin after the pretreatment at this time was 97 mol%, and the proportion of hydrogen ions was 3 mol%. The measurement results of the metal impurity contents are each shown in Tables 7 and 8.

[0092]

Comparative Example 5