Regeneration technology of tetramethylammonium hydroxide using ion exchange resin

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Abstract

Tetramethylammonium hydroxide is used in various electric and electronic parts production processes, such as those for making semiconductors, liquid crystal displays and printed circuit boards. The discharged amount of this chemical reaches about 2,500 ton/year from one factory in Japan. The waste liquor discharged from the liquid crystal display production contains 0.53 wt% tetramethylammonium hydroxide, 60 mg/dm^3 phenol and a ppb order of metal ions. In the cation exchange reaction, tetramethylammonium ion is captured on the cation exchange resin. Other non-ionic organic matter, such as phenol, goes through the resin without being captured on it, the separation being attained in this step. In the elution step, tetramethylammonium ion captured on the resin is released as tetramethylammonium chloride into aqueous solution by the action of dilute hydrochloric acid. Tetramethylammonium chloride is converted to tetramethylammonium hydroxide by the reaction between tetramethylammonium chloride and OH type anion exchange resin. The process is composed of three steps, that is, cation exchange, elution and conversion. The experiments were carried out using an ion exchange resin column of 20 mmϕ and 735 mm height, in order to investigate the recovery and purity of percents tetramethylammonium hydroxide at each step.

1. Introduction

Tetramethylammonium hydroxide (TMAH) is used in various electric and electronic parts production processes, such as those for making semiconductors, liquid crystal displays and printed circuit boards. The discharged amount of this chemical reaches about 2,500 ton/year from one factory in Japan. The waste liquor contains a lot of organic matter, which means high BOD and COD(1). The TMAH waste solution is treated either by means of an evaporation concentration method or by an incineration method. However, these methods cause some engineering problems: high cost, high environmental load, and so on. The development of a new method with which to recover pure TMAH from the waste TMAH solution is urgently wanted both the viewpoint of resource recycling and that of global environmental protection[2)-4)]. In this study, the separation and removal of TMAH were investigated using an ion exchange resin method from a TMAH solution and an artificial TMAH waste solution containing phenol, which is a model material of organic materials

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dissolved from photoresist.

2. Experimental

TMAM Recovery Process Using an Ion Exchange Resin Method

The regeneration treatment process of a TMAH waste solution and the separation principle of TMAH are shown in **Figs.1, 2** and **3**. The separation of TMA^+ and phenol in the waste TMAH solution can be achieved by causing a cation exchange reaction between TMA^+ and an H^+ type cation exchange resin. The cation exchange reaction is expressed as,

$$TMA^{+}+OH^{-}+H^{+}\text{-resin} \rightarrow TMA^{+}\text{-resin}+H_2O$$

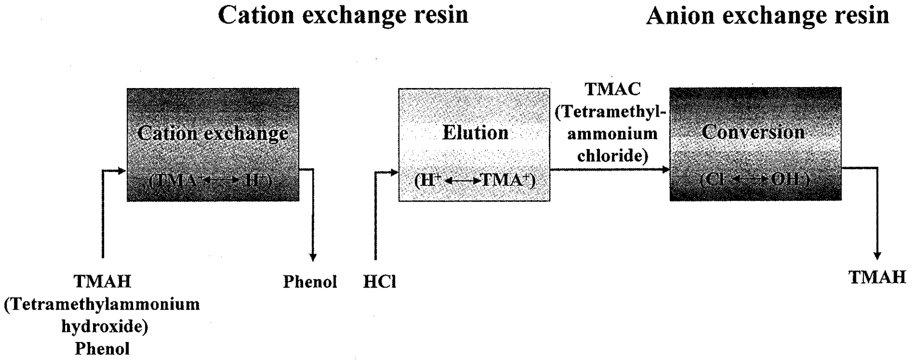

Fig.1 Recovery process of TMAH

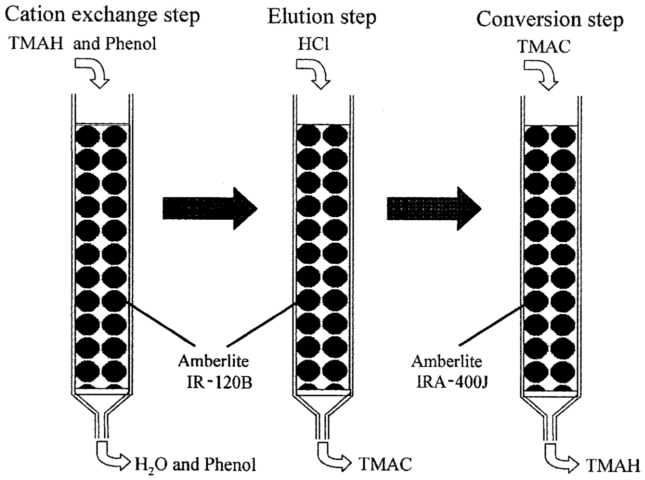

Fig.2 Recovery and conversion methods

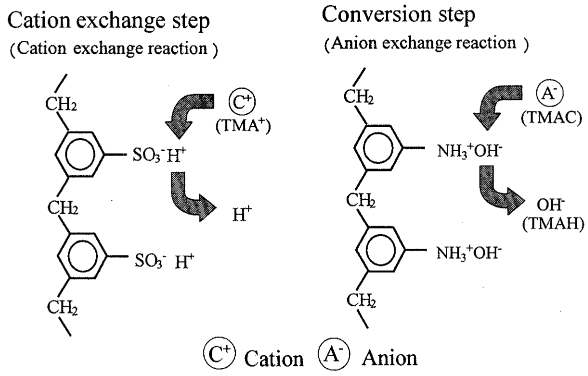

Fig.3 Mechanism of regeneration of TMAH

Washing of the cation exchange resin column with water is required in order to remove the TMAH waste solution remaining in the resin bed. It is necessary to wash the cation exchange resin adequately in order to ensure the purity of TMAH. The TMAH captured in the cation exchange resin is detached in the elution step. When HCl solution is used as an eluent, TMA^+ is eluted as a form of tetramethylammonium chloride (TMAC). The elution reaction is shown by,

$$TMA^+\text{-resin} + H^+ + Cl^- \rightarrow TMA^+ + Cl^- + H^+\text{-resin}$$

In the next step, the TMAC effluent solution obtained in the previous step is introduced into the column of OH^- type anion exchange resin, in order to convert TMAH from TMAC with an exchange reaction between Cl^- in aqueous solution and OH^- in the resin. The anion exchange reaction is expressed by

$$TMA^+ + Cl^- + OH^-\text{-resin} \rightarrow TMA^+ + OH^- + Cl^-\text{-resin}$$

Regeneration of TMAH is carried out by means of the cation exchange, washing, elution and anion exchange steps.

Amberlite IR-120B and Amberlite IRA-400J are used after regeneration to H^+ type and OH^- type, respectively. Regeneration is carried out by contacting the Amberlite IR-120B with a 1.0 mol/dm^3 HCl solution and the Amberlite IRA-400J with a 1.0 mol/dm^3 NaOH solution. The ion exchange column was made of glass with a 739mm height and 20mm diameter. The artificial solution was prepared by dissolving TMAH and phenol at a suitable concentration. The solution was passed through the resin column as a downward stream, and the effluent was subsequently collected by a fraction collector. The concentrations of TMA^+ and Cl^- were determined by an ion chromatograph.

The experimental apparatus and experimental conditions of the ion exchange operation in each step are shown in **Fig.4** and **Table 1**.

3. Results and Discussion

Cation exchange velocity of TMA^+ with H^+ type cation exchange resin (Amberlite IR-

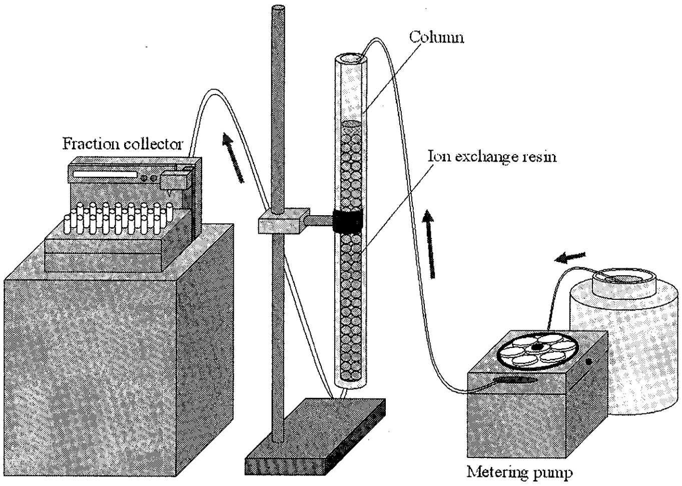

Fig.4 Experimental apparatus

Table 1. Experimental condition

	Cation exchange	Elution	Conversion
Space Velocity [h^{-1}]	**10**	**10**	**10**
Bed volume [cm^3]	**48**	**48**	**70**
Bed height [cm]	**15.5**	**16.3**	**21.5**

120B) in a batch exchange test is shown in **Fig.5**. The cation exchange velocity of TMA^+ reaches an equilibrium value within 5 min, and the velocity is rather quick. The velocity obtained in the batch test is important for determining the effluent velocity in the column method. In the case of the column method, space velocity (SV) is used as the effluent velocity. From the result in Fig.5, the effluent velocity is determined to be SV 10, which corresponds to a residence time of 6 min$^{5)}$.

The breakthrough curve for TMA^+ in the cation exchange column and the pH of effluent are shown in **Fig.6**, using the cation exchange resin, IR-120B. In the case of a 29.3 mmol/dm^3 TMAH initial concentration, the breakthrough point of TMA^+ appears at 3,200 cm^3 of effluent volume, and the pH of eluent changes remarkably at this breakthrough point. The rapid change in pH means that H^+ is not released from the cation exchange resin, because the H^+ type cation exchange resin is already saturated with TMA^+. In the region before the breakthrough point, the total exchange amount of TMA^+ is 93.6 mmol. The effluent volume of 3,200cm^3, at which the breakthrough point appears, is about 67 times the bed volume (wet resin volume), and the bed volume value is one of the yardsticks by which

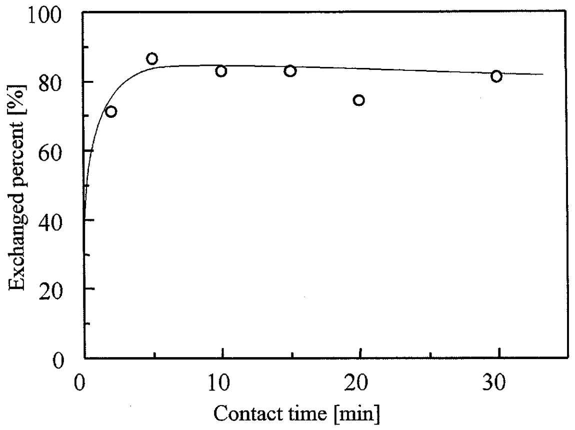

Fig.5 Batch test for cation exchange velocity of TMA$^+$ with Amberlite IR-120B

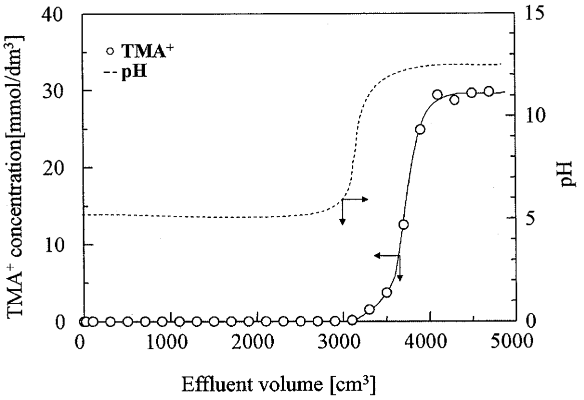

Fig.6 Breakthrough curve of TMA$^+$ with Amberlite IR-120B
Initial TMA$^+$ conc. : 2267ppm

to show the performance of this cation exchange operation.

A distribution diagram of phenol species in aqueous solution is shown in **Fig.7** as a function of pH. Phenol in aqueous solution exists as a form of neutral molecule or anionic species. Figure 7 reveals that the anionic species of phenol is predominant in the pH region

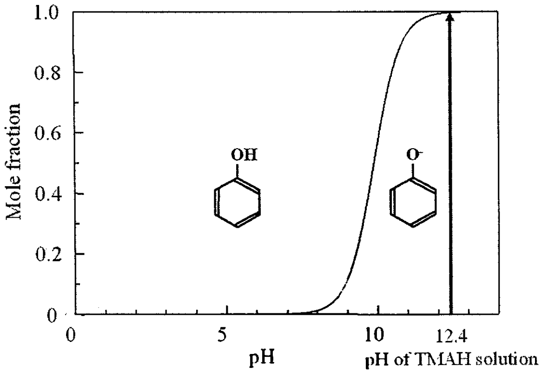

Fig.7 Distribution diagram of phenol species as a function of pH

whose value is over 10. The pH of typical TMAH waste solution is 12.4, and, at this pH, phenol exists as an anionic species. Therefore, phenol species are not captured by the cation exchange resin, and these components pass through the cation exchange resin column.

Figure 8 shows the breakthrough curve for the TMAH artificial waste solution containing 30.3 mmol/dm^3 of TMAH and 200 ppm of phenol. Phenol is not captured by the cation exchange resin, and it passes through this column. The breakthrough point of TMA$^+$ appears at an effluent volume of 3,200 cm^3, and the amount of TMA$^+$ exchange is about 95.0 mmol before the breakthrough point. The breakthrough points in Figs.7 and 8 are almost the same, regardless of the existence of phenol.

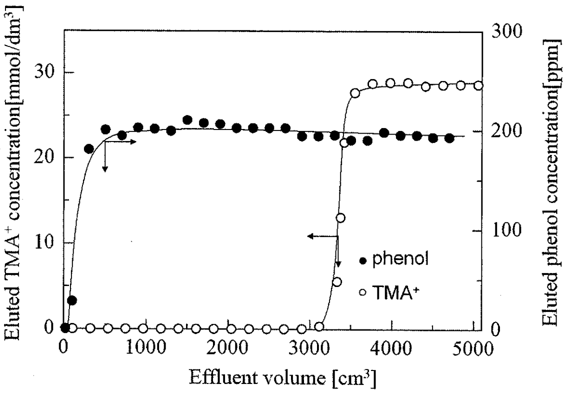

Fig.8 Breakthrough curve of TMA$^+$ and phenol with Amberlite IR-120B for binary solution

The results of washing the cation exchange column with water are shown in **Fig.9**. The objective of this washing step is to remove the TMAH waste solution remaining in the resin column. The washing step is necessary in order to keep the purity of recovered TMAH high. Perfect washing with water is already achieved at 286 cm^3 of effluent volume, this amount of effluent being 6 times that of the wet resin volume.

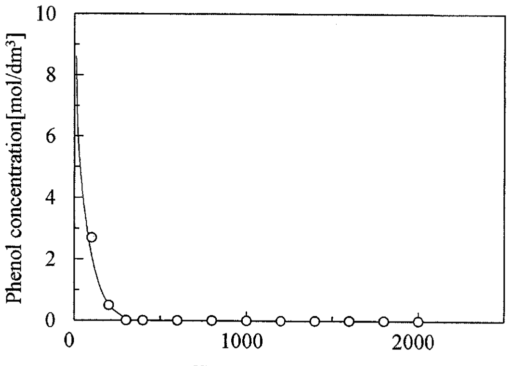

Fig.9 Washing of feed solution from resin column by water

Elution curves of TMAC with HCl solutions of various concentrations are shown in **Fig.10**. TMA^+ is released as TMAC from the cation exchange resin between TMA^+ in the resin and H^+ in solution. When an aqueous solution containing high HCl concentration is used, the elution curves becomes sharp, and TMAC of a high concentration can be obtained with a small amount of HCl solution. A decrease in HCl concentration causes low concentration of obtained TMAC as well as large volume of obtained TMAC solution. For example, the elution of TMA^+ completes at 410cm^3 of effluent volume and the amount of recovered TMAC is 83.6 mmol in the case of 1.0 mol/dm^3 HCl.

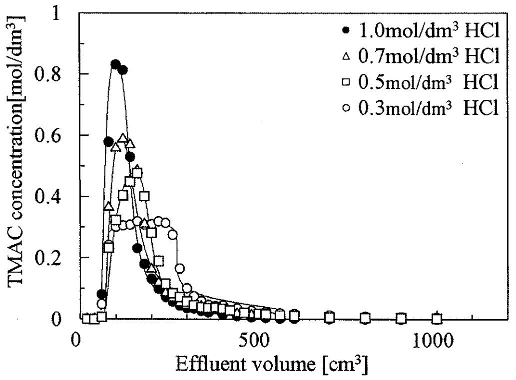

Fig.10 Elution curves of TMAC (tetramethylammonium chloride) with HCl solution from Amberlite IR-120B

Figure 11 shows the pH of effluent in the elution process. From these results we can see that it is not suitable to pass a large amount of eluent, HCl, through this elution column, because this leads to contamination of TMAC with HCl in the eluent.

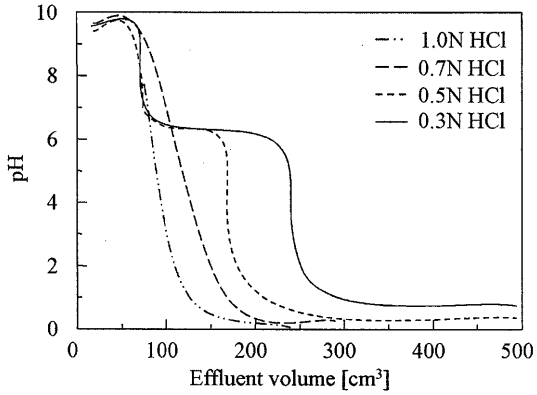

Fig.11 pH change in elution step

The anion exchange reaction between Cl^- in TMAC solution and OH^- in the anion exchange resin Amberlite IRA-400J, is conducted by passing the TMAC solution, which is obtained in the previous elution step, through the anion exchange resin column. The performance of the anion exchange operation is shown in **Fig.12**. The conversion from TMAC to TMAH can be achieved by this operation. The conversion reaction is expressed as

$$TMA^{+}+Cl^{-}+OH^{-}\text{-resin} \rightarrow TMA^{+}+OH^{-}+Cl^{-}\text{-resin}$$

When a TMAC solution of 0.1 mol/dm^3 is passed through the anion exchange column, the breakthrough point of Cl$^-$ appears at 670 cm^3 of effluent volume. Contamination of TMAC with HCl in the elution step causes a decline of TMAH purity according to the following:

$$TMA^{+}+Cl^{-}+OH^{-}\text{-resin} \rightarrow TMA^{+}+OH^{-}+Cl^{-}\text{-resin}$$

$$H^{+}+Cl^{-}+OH^{-}\text{-resin} \rightarrow H_2O+Cl^{-}\text{-resin}$$

At 670cm^3 of effluent volume the recovery amount and conversion to TMAH are 66.8 mmol and 79.9%, respectively.

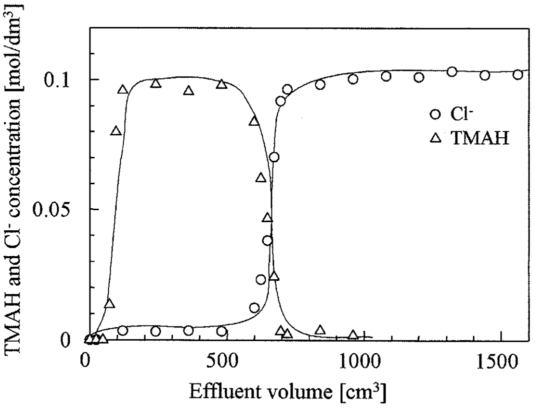

Fig.12 Conversion of TMAC to TMAH using OH$^-$ type anion exchange resin (Amberlite IRA-400J)

The change in pH of effluent in the anion exchange step (namely, conversion step) is shown in **Fig.13**. The pH of effluent rapidly changes at 670 cm^3 of effluent volume, at which conversion or regeneration is already completed. **Figure 14** shows the recovered amount, recovery percent, conversion percent during each step, and the overall yield of TMAH through a series of treatment steps. The total recovery of TMAH in cation exchange and elution steps is 89.4% (83.6 / 93.6 × 100% = 89.4%), and the TMAH conversion rate is 79.9% (66.8 / 83.6 × 100% =79.7%). The overall yield of TMAH through the whole series of treatment steps is 71.4%. From the above mentioned results, it can be seen that TMAH can be recovered and regenerated from the TMAH waste solution by using two kinds of ion exchange resins.

4. Conclusions

The separation and recovery of TMAH from a waste TMAH solution containing phenol were investigated using an ion exchange resin method. The process comprises of three

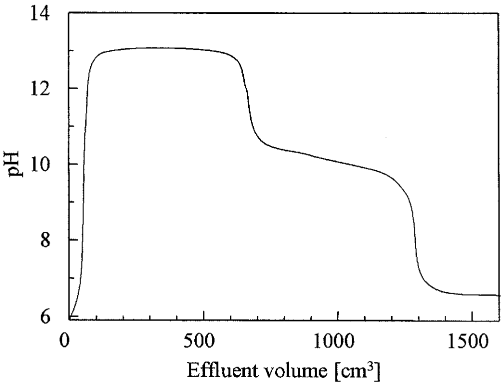

Fig.13 pH change in conversion step

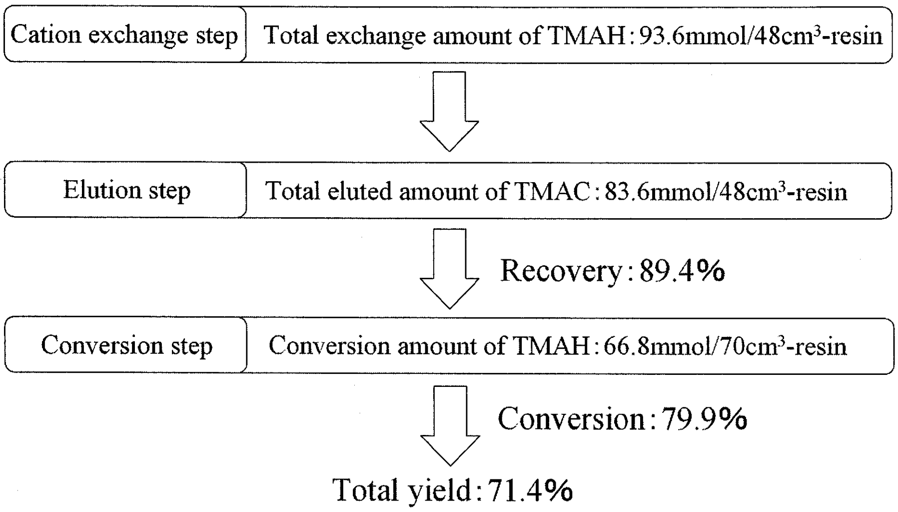

Fig.14 Recovery process of TMAH using cation exchange resin (Amberlite IR-120B) and anion exchange resin (Amberlite IRA-400J)

steps: cation exchange, elution, and conversion. In the cation exchange step, a TMAH waste solution of up to 67 times that of bed volume can be treated. Washing of cation exchange resin after TMA^+ adsorption is adequately effected with water of 6 times bed volume. In the elution step, the concentration of obtained TMAC increases with increasing HCl concentration, but an increase in HCl concentration at the same time leads to the load on the next conversion step. Conversion of TMAH at the breakthrough point is 79.9%. The total recovery of TMAH in cation exchange and elution steps was 89.4%, the conversion of TMAH was 79.9% and the overall yield of TMAH through a series of treatment steps was 71.4%, respectively. The TMAH can be removed and regenerated from the TMAH waste solution using two kinds of ion exchange resin.

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