

# RECOVERY OF PHOSPHORIC ACID FROM WASTE ACID MIXTURE WITH SOLVENT EXTRACTION

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## Abstract

By applying a solvent extraction method for the etching waste solution discharged from the manufacturing process of liquid crystal display, the removal of acetic acid and nitric acid were carried out from the waste acid mixture containing phosphoric, acetic and nitric acids to obtain phosphoric acid as the raffinate. Fundamental studies on the recovery of phosphoric acid were conducted by using Tri-octyl phosphate (TOP) as the extractant for acetic acid and nitric acid. From the results, demonstration tests using a mixer-settler equipment were carried out to obtain crude phosphoric acid.

Acetic and nitric acids were selectively extracted by TOP from the waste acid mixture, which contains phosphoric acid as a main component. From the McCabe Thiele analysis, almost all of the acetic and nitric acids were removed by a countercurrent multi-extraction operation of phase ratio (A/O) 0.4 and 6-stage. When TOP loading acids was contacted with the water under the countercurrent operation conditions of phase ratio (O/A) 1.0 and 4-stage, 99% of acetic acid and 99.5% of nitric acid were stripped from the organic phase, respectively. From these results obtained by the fundamental studies, a demonstration test was carried out for the extraction of acetic and nitric acids by using a mixer-settler equipment. Consequently, the extractions of acetic and nitric acids in the waste acid mixture were about 95% and 98%, respectively, and crude phosphoric acid can be obtained as a raffinate after the solvent extraction.

## 1. Introduction

Phosphoric acid is used in manufacturing a liquid display and a semi conductor. The manufacturing process of a liquid crystal display consists of many steps, such as vapor deposition, resist coating, exposure, photofinishing, etching, resist removal and scrubbing. For example, acid mixtures containing acetic acid, nitric acid and phosphoric acid are used in the etching process to dissolve aluminum-molybdenum alloy and silver deposited on the glass plate. The waste solution discharged from this process contains acids and metal ions such as aluminum and molybdenum. The amount of waste acid discharged from the case study factory is estimated to be about 3,000 tons per year. Conventionally, a neutralization method is applied to the waste acid treatment.

In the neutralization method, calcium hydroxide is added to the waste acid mixture to

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form insoluble calcium phosphates. Acetate ions and nitrate ions, which remain in the waste solution after a neutralization method, are removed in the activated sludge process. This method, however, still has many outstanding engineering problems such as high cost for neutralization and sludge disposal. From the environmental viewpoints, it is important to develop the technology by which each acid is separated and recovered from the waste acid mixture.

Membrane separation, ion exchange resin and solvent extraction are considered as the recovery method of acid from waste acid mixture. The membrane separation method gives high recovery and purity for each acid, but there are many problems such that the membrane and equipment are expensive and the operation is complex. The ion exchange resin method with anion-exchange resin cannot be applied for the acid recovery of high concentration, because its exchange capacity is small and it is only applicable to low concentrations. On the other hand, the solvent extraction method is applied to the waste acid mixture because it is a closed system, a continuous operation and low cost. The Nisshin process developed by Nisshin Steel Co., Ltd.<sup>1)</sup>, the Kawatetsu process by Kawasaki Steel Co., Ltd.<sup>2)</sup> and the AX process from Sweden<sup>3)</sup> have tried to apply for the acid mixtures of nitric acid and hydrofluoric acid. They are the treatment technology for the waste acid mixture generated in the pickling process of steel. The research of solvent extraction and extraction characteristics has been published for the single component of acetic, nitric and phosphoric acids and two component system of nitric and phosphoric acids<sup>4)</sup>. However, there has been no research on solvent extraction for three component system of phosphoric, acetic and nitric acids.

The objective of this study is the basic study and application of solvent extraction for the separation of acid mixtures in order to reuse phosphoric acid in the etching waste in a manufacturing process of liquid crystal display. The extractant concentration and the operation conditions are examined through beaker experiments in order to estimate the optical condition of the extraction and stripping to achieve fine separation. Based on the experimental results obtained in our fundamental studies, demonstration tests of the extraction and stripping of acetic, nitric and phosphoric acids in the waste acid were carried out by using a bench scale mixer-settler extraction equipment.

## 2. Experimental

### 2.1. Fundamental study

Tri-octyl phosphate (TOP) was supplied by Wako Pure Chemical Industries, Ltd. as an extractant and Solvesso 150 which was bought from Touei Industry, Ltd. was used as a diluent. The artificial waste acid mixture was prepared by using acetic, nitric and phosphoric acids, which were supplied by Wako Pure Chemical Industries, Ltd.. The concentration of each acid in the artificial waste acid mixture is shown in Table 1.

TOP was diluted to 50vol% with Solvesso 150 for the organic phase. The single component of acetic, nitric and phosphoric acids and the above-mentioned acid mixture were used as the aqueous phase. In the extraction experiments for each acid in the single

CH <sub>3</sub> COOH	HNO <sub>3</sub>	H <sub>3</sub> PO <sub>4</sub>
0.754 [mol/dm <sup>3</sup> ]	0.229 [mol/dm <sup>3</sup> ]	5.82 [mol/dm <sup>3</sup> ]
3.4 [wt%]	1.1 [wt%]	43.3 [wt%]

Table 1. Chemical composition of waste acid mixture used in beaker test

component solution, 15cm<sup>3</sup> of the organic and aqueous phases were fed to a centrifuge tube and then the tube was shaken by a vertical shaker. The stripping experiments were carried out at a phase ratio (O/A) of 0.5-2. The extraction experiments of the acid mixture were conducted either in the centrifuge tube or in the separating funnel under the conditions of phase ratio (A/O) 0.1-10. The phase ratio (O/A) in the stripping experiments was changed from 0.1 to 10. The acid concentrations in the aqueous phase after the extraction were measured by using an automatic potentiometric titrator (Kyoto Electronics Manufacturing Co., Ltd, AT-510) and an ion chromatograph (Dionex Co., Ltd, DX-500).

## 2. Performance tests with mixer-settler equipment

The capacities of the mixer and settler parts of a mixer-settler equipment is approximately 600cm<sup>3</sup> and 1,800cm<sup>3</sup>, respectively. The organic and aqueous phases were conveyed with the suction action of the stirring blade positioned in the bottom of the mixer. The composition of each acid in the artificial waste acid mixture used in a demonstration test is shown in Table 2. In the extraction experiments, the flow rate of the organic and aqueous phases, and the flow ratio (A/O) were set to be 23.9cm<sup>3</sup>/h, 8.10cm<sup>3</sup>/h and 0.34, respectively. In the stripping experiments, the flow rate of the organic and aqueous phases, and the flow ratio (O/A) were determined to be 18.7cm<sup>3</sup>/h, 19.9cm<sup>3</sup>/h and 0.94, respectively. The organic and aqueous phases were sampled from each stage of the settler part of the

CH <sub>3</sub> COOH	HNO <sub>3</sub>	H <sub>3</sub> PO <sub>4</sub>
0.626	0.182	4.58

Table 2. Chemical composition of waste acid mixture used in mixer-settler test [mol/dm<sup>3</sup>]

mixer-settler equipment. The concentrations of each acid of the aqueous phase were measured by an ion chromatograph. The loading organic phase was twice contacted with pure water at a phase ratio (O/A) of 0.5 in order to transform the acids to aqueous phase. The acid concentrations of the organic phase were calculated from the difference between the initial and equilibrium acid concentrations in aqueous phase.

## Results and discussion

### 1. Extraction and stripping tests for a single component system of acetic and nitric acids and a three component system

Tri-alkyl phosphates like TOP and Tri-n-butyl phosphate (TBP), and alcohols like 2-ethylhexyl alcohol are useful to extract acetic acid. TBP selectively exhibits a high extraction of nitric acid<sup>5)</sup>. Elsewhere, we have reported that 2-ethylhexyl alcohol is effective for the extraction of acetic acid and that TBP is superior for the extraction of nitric acid<sup>6)</sup>. Little research has been published on the extraction of acetic and nitric acids with TOP.

Our study examined the extraction separation of acetic and nitric acids from phosphoric solution with high extraction. When acetic acid concentrations in an equilibrium aqueous solution are 0.0635-0.307mol/dm<sup>3</sup> for a single component system, the distribution coefficient D has the value range of 0.508-0.307. The distribution coefficient D is defined as follows,

$$D=y/x \quad (1)$$

in which x and y denote the acid concentration in the equilibrium aqueous and organic phases. The extraction and stripping isotherms of acetic acid for the single component system are expressed by the following regression equation, as they overlap each other,

$$y=-0.1585x^2+0.5184x \quad (R^2=0.9953) \quad (2)$$

Similarly, the extraction and stripping isotherms of nitric acid for the single component system are represented by the following regression equation,

$$y=-0.2001x^2+0.0146x \quad (R^2=0.9940) \quad (3)$$

When nitric acid concentrations in the equilibrium aqueous solution are 0.0463-0.4670mol/dm<sup>3</sup>, the distribution coefficient D shows the value range of 0.0239-0.108.

The extraction isotherms of acetic and nitric acids in the extraction from the waste acid containing phosphoric acid are shown in Fig. 1. Nitric and acetic acids are extracted with TOP simultaneously. In Fig. 1, because the concentration of nitric acid in the organic phase is higher than that of acetic acid, the extractability of nitric acid with TOP for the three component system is superior to that of acetic acid. The extraction amount of acetic and nitric acids increases clearly compared with that for the single component system. When there is a lot of phosphoric acid in the aqueous phase, the following phenomena take place: 1) the amount of water in the aqueous phase decreases and 2) the dissociation of nitric acid is depressed with an increase in hydrogen ion. The extraction amounts of both of acetic and nitric acids are increased by the phenomenon 1), while the phenomenon 2) acts so that the

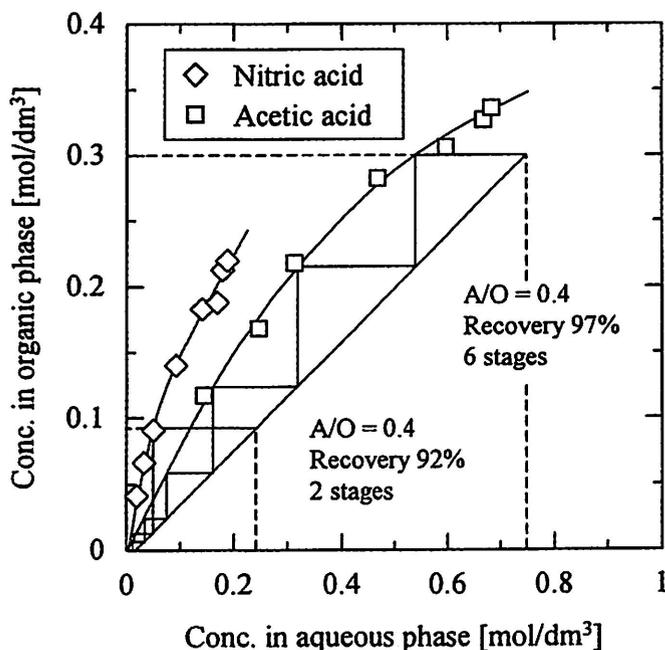


Fig.1 Extraction isotherms of acetic and nitric acids in waste acid mixture with 50vol% TOP in solvesso 150

extraction amount of nitric acid may increase due to dissociation degree of nitric acid. The reason for the increase in the extraction of acetic and nitric acids for the three component system is explained by the above phenomena. On the other hand, any phosphoric acid is hardly extracted.

In order to obtain the theoretical stage number in a countercurrent multi-stage operation for the extraction of acetic and nitric acids, McCabe-Thiele analysis was applied to the extraction isotherm. When the concentrations of acetic acid in the inlet aqueous phase and those in the outlet organic phase, and the recovery of acetic acid are assumed to be  $0.754 \text{ mol/dm}^3$ ,  $0.3 \text{ mol/dm}^3$  and 97%, respectively, the phase ratio (A/O) and the required theoretical stage number are determined to be 0.4 and 6-stage. The above analysis is also carried out for nitric acid. Under the operation conditions of the phase ratio of 0.4 and the extraction stage of 6, the concentration of nitric acid in the raffinate and the recovery are  $0.0011 \text{ mol/dm}^3$  and 99.5%, respectively. Then, the outlet concentration of nitric acid in the organic phase becomes  $0.09 \text{ mol/dm}^3$ . The stripping isotherms from the organic phase loading acetic and nitric acids with water are shown in Fig. 2. McCabe-Thiele analysis was applied to obtain the theoretical stage number required for stripping of acetic and nitric acids according to the same procedure conducted for the extraction stage. When the concentration of acetic acid in the inlet organic phase, the concentration of acetic acid in the outlet aqueous phase and the recovery of acetic acid are assumed to be  $0.3 \text{ mol/dm}^3$  and 99%, a phase ratio (O/A) and the theoretical stage number are determined to be 1.0 and 4-stage. The above analysis is carried out for stripping of nitric acid as the same way. Under the conditions of a phase ratio of 1.0 and the stripping stage of 4 for stripping of nitric acid, the recovery and the concentration of nitric acid in the outlet aqueous phase become 99.5%

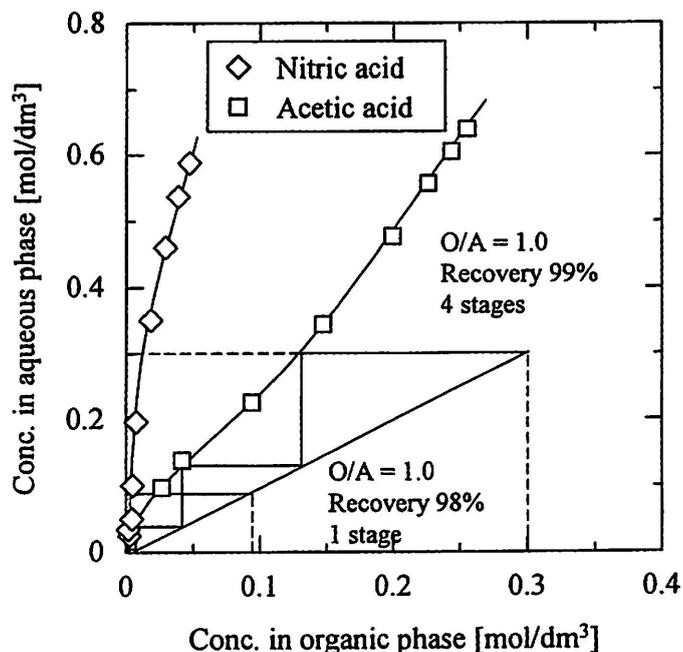


Fig.2 Stripping isotherms of acetic and nitric acids from 50vol% TOP in solvesso 150 with water and 0.09mol/dm<sup>3</sup>, respectively.

From the above beaker test results, it may be conducted that 6-stage countercurrent extraction with phase ratio of 0.4 and 4-stage countercurrent stripping with phase ratio of 1.0 are required to recover phosphoric acid as extraction raffinate and to separate acetic and nitric acids from phosphoric acid.

## 2. Extraction and stripping tests with a mixer-settler equipment

A flowsheet for the extraction and stripping processes of acetic and nitric acids is shown in Fig. 3. In the extraction process, the inlet organic phase is set to the 1st stage and the inlet aqueous phase is set to the 6th stage. In the stripping process, the inlet organic phase and the inlet aqueous phase are set to 1st stage and 4th stage, respectively. Continuous extraction and stripping tests were carried out under the above conditions by using a mixer-settler equipment.

The concentration changes in acetic, nitric and phosphoric acids in each stage organic phase in the extraction and stripping processes are shown in Fig. 4. The values of the 0th stage and the 6th stage in the figure respectively represent the acid concentrations of the feed organic phase and the outlet organic phase. In the extraction process, the concentrations of acetic and nitric acids increase with an increase in the stage number, and then the concentrations of the outlet organic phase become 0.18mol/dm<sup>3</sup> and 0.063mol/dm<sup>3</sup>, respectively. The concentration of phosphoric acid in the 1st stage is approximately 0.025mol/dm<sup>3</sup>, and after that it hardly changes. In the stripping process, the concentration of

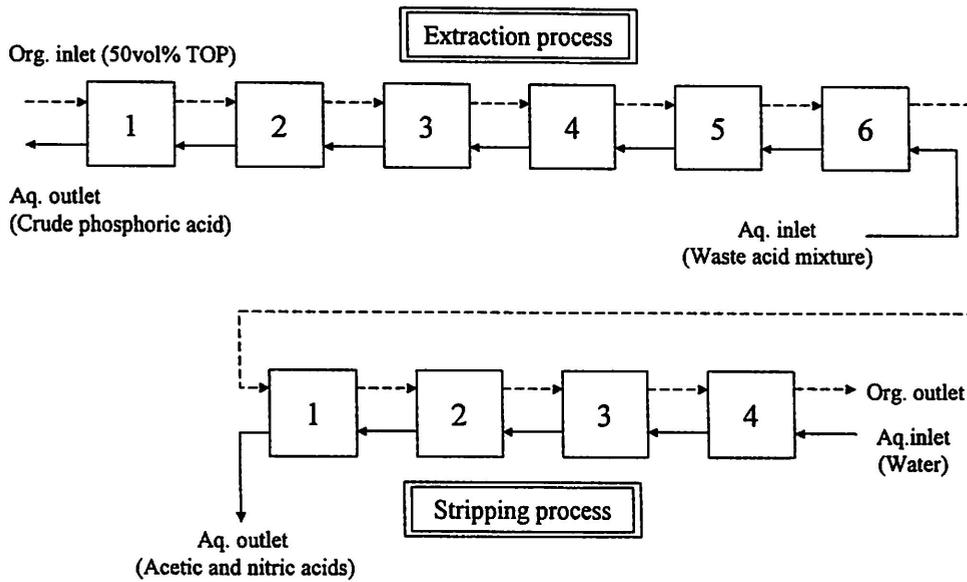


Fig.3 Flowsheet of continuous countercurrent multi-stages operation

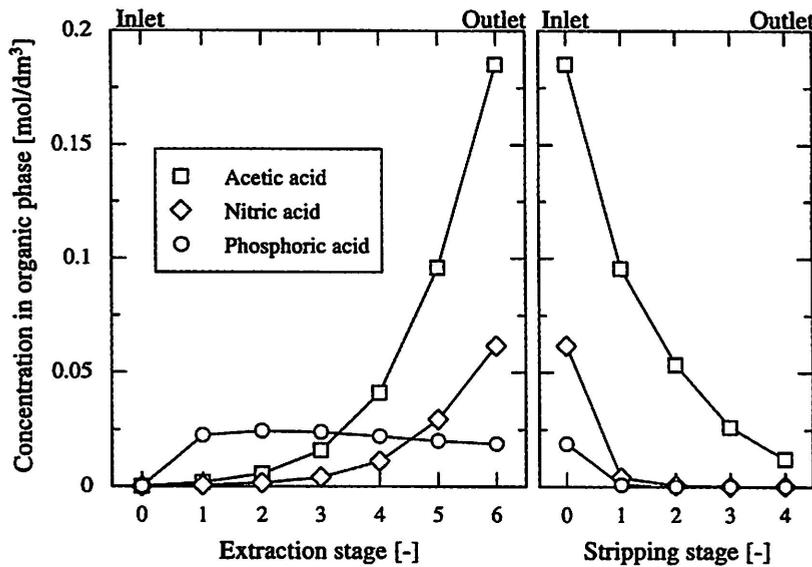


Fig.4 Change in concentrations of acetic, nitric and phosphoric acids in organic phase through extraction and stripping stages (Org. phase : 50vol% TOP diluted in solvesso 150)  
 Extraction : aq. phase = 8.10 dm<sup>3</sup>/hr, org. phase = 23.9dm<sup>3</sup>/hr(A/O = 0.34)  
 Stripping : aq. phase = 19.9 dm<sup>3</sup>/hr, org. phase = 18.7dm<sup>3</sup>/hr(O/A = 0.94)

acetic acid decreases with an increase in the stage number, and acetic acid remains in the organic phase at a concentration of 0.01mol/dm<sup>3</sup> after the 4-stage stripping process. It is necessary to increase the stripping stages in order to improve the stripping of acetic acid. Nitric and phosphoric acids, however, hardly exist in the organic phase after the stripping of the two stages. The concentration change in acetic, nitric and phosphoric acids in the

aqueous phase during the extraction and stripping processes is shown in Fig. 5. The values of the 7th stage of the extraction and the 5th stage of the stripping processes represent the acid concentration in the inlet aqueous phase. The concentration of acetic and nitric acids decreases with the number of extraction stage and the outlet concentrations of acetic and nitric acids become less than  $0.02\text{mol/dm}^3$  and  $0.001\text{mol/dm}^3$ , respectively. The concentration

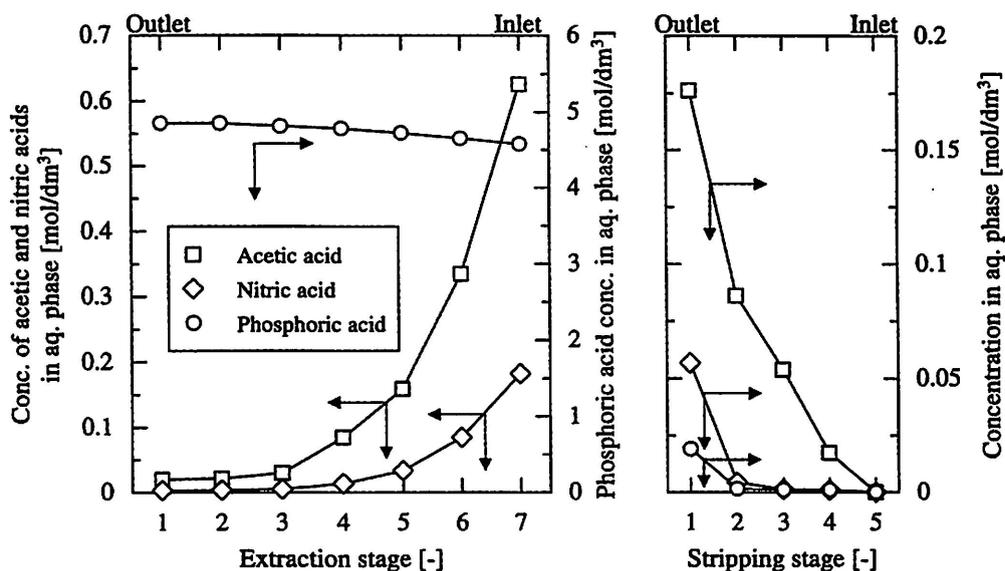


Fig.5 Change in concentrations of acetic, nitric and phosphoric acids in aqueous phase through extraction and stripping stages (The operating conditions are the same as those in Fig.4)

of phosphoric acid increases slightly in the outlet of the extraction process, and its value is approximately  $4.8\text{mol/dm}^3$ . Although the reason why the increase in phosphoric acid concentration has not been clarified, it is considered that the phosphoric acid loaded in the organic phase affects the extraction of acetic and nitric acids in the stripping process. The concentrations of all acids increase with the number of stripping stages in the stripping process. After a 4-stage stripping operation, the concentrations of acetic, nitric and phosphoric acids in the aqueous phase are approximately  $0.175\text{mol/dm}^3$ ,  $0.055\text{mol/dm}^3$  and  $0.02\text{mol/dm}^3$ , respectively. The acid concentration of each stage in the extraction and stripping processes is converted into the extraction and the stripping in the Fig. 6. At a countercurrent extraction of the 6-stage, the extraction of acetic and nitric acids are approximately 95% and 98%, respectively. On the other hand, the extraction of phosphoric acid is only 1.5%. In a similar way, the stripping by a countercurrent operation gives an extraction of 92% for acetic acid and those of almost 100% for nitric and phosphoric acids.

When the flow ratio (A/O) and the number of stages are set at 0.34 and 6-stages by a countercurrent extraction operation, about 95% and 98% of extractions for the acetic and nitric acids in aqueous phase are obtained. Extraction of phosphoric acid is approximately 1.5% and the concentrations of acetic, nitric and phosphoric acids in the raffinate are  $0.02\text{mol/dm}^3$ , below  $0.001\text{mol/dm}^3$  and  $0.48\text{mol/dm}^3$ , respectively. When a countercurrent

multi-stripping operation with the water is applied to the loaded organic phase in the flow ratio (O/A) 0.94, the stripping of acetic acid is approximately 92% and nitric and phosphoric acid are completely stripped at the 2nd stage and the 1st stage, respectively.

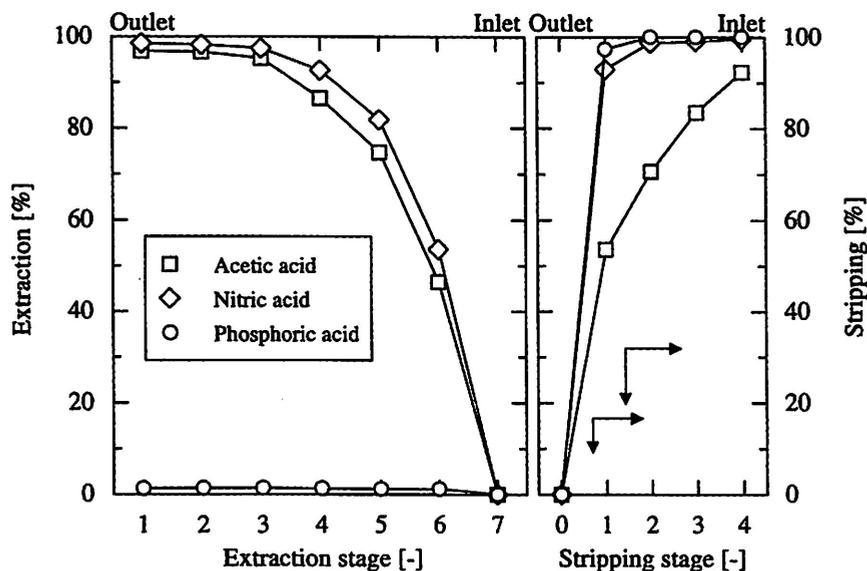


Fig.6 Extraction and stripping behavior of acetic, nitric and phosphoric acids in aq. phase with mixer-settler equipment (The operating conditions are the same as those in Fig.4)

#### 4. Conclusions

By applying the solvent extraction method for artificial waste acid discharged from the manufacturing process of liquid crystal display, the removal of acetic and nitric acids from the acid mixture containing phosphoric acid as main component is performed in order to obtain crude phosphoric acid. For the extraction and stripping results of phosphoric, acetic and nitric acids, a demonstration test was carried out by using a mixer-settler equipment.

TOP selectively extracts acetic and nitric acids from the waste acid mixture and it does not extract phosphoric acid. McCabe-Thiele analysis is carried out for the extraction isotherms. By a countercurrent operation of a phase ratio (A/O) 0.4 and 6-stage, the acetic acid in the waste is extracted in  $0.48\text{mol}/\text{dm}^3$  of the concentration with 97% of the recovery with 50vol% TOP. Under the condition of a phase ratio (A/O) 0.4 and 4-stage extraction operation, nitric acid is extracted with 99.5% of recovery in  $0.48\text{mol}/\text{dm}^3$  of the concentration in the organic phase.

The extraction and stripping tests of acetic and nitric acids in the waste acid mixture were carried out by using a mixer-settler equipment. By a countercurrent extraction of the flow rate (A/O) and 6-stage, the concentrations of acetic, nitric and phosphoric acids are  $0.18\text{mol}/\text{dm}^3$ ,  $0.063\text{mol}/\text{dm}^3$  and  $0.025\text{mol}/\text{dm}^3$  in the organic phase, respectively. The concentrations of acetic, nitric and phosphoric acids in the raffinate are about  $0.02\text{mol}/\text{dm}^3$ ,

0.001mol/dm<sup>3</sup> and 4.8mol/dm<sup>3</sup>, respectively. When these values are expressed as form of extraction, they are approximately 95%, 98% and 1.5%, and the high separation can be achieved to obtain crude phosphoric acid. In a countercurrent stripping of the flow ratio (A/O) 0.94 and 4-stage operation the concentration of acetic acid in the outlet of organic phase is about 0.01mol/dm<sup>3</sup> and the concentrations of nitric acid and phosphoric acid are almost 0mol/dm<sup>3</sup>. The each acid concentration in the outlet of aqueous phase was approximately 0.175mol/dm<sup>3</sup>, 0.055mol/dm<sup>3</sup> and 0.02mol/dm<sup>3</sup>, respectively. The strippings of acetic, nitric and phosphoric acids are approximately 92%, 100% and 100%. From these results, the removal process of acetic and nitric acids obtained in beaker test is demonstrated by the above mixer settler test.

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