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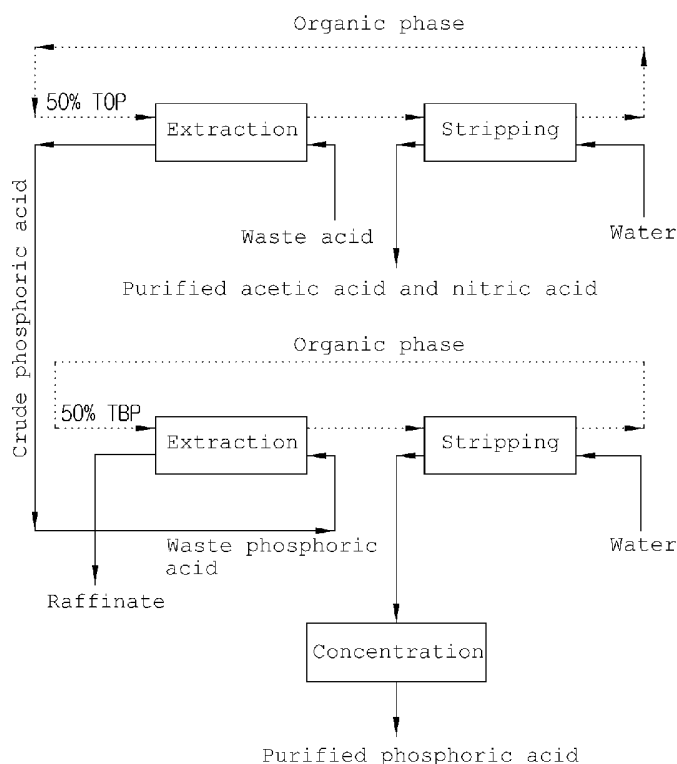
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[Continued on next page]

(54) Title: METHOD FOR TREATING OF ETCHING ACID WASTE CONTAINING PHOSPHORIC ACID, ACETIC ACID AND NITRIC ACID



(57) Abstract: The present invention relates to a method for treating an etching waste with tri-octyl-phosphate (TOP) and tri-butyl-phosphate (TBP) as organic extraction solvents and more particularly, a method for treating an etching waste from the production process of liquid crystals to recover acids from the etching waste by means of solvent extraction comprising: a phase separation process of contacting the tricomponent waste solution (aqueous) comprising phosphoric acid and acetic acid, nitric acid or a mixture thereof with a diluted organic phase comprising tri-octyl-phosphate (TOP) and a diluent at a predetermined volume ratio, followed by uniformly stirring and standstill to separate an extract phase containing the selectively extracted acetic acid and nitric acid and raffinate comprising phosphoric acid remaining in the waste solution; a separation process of stripping the acetic acid and nitric acid from the separated extract phase with water to recover the acids; and a phosphoric acid recovery process of extracting phosphoric acid remaining in the raffinate with an organic phase comprising tri-butyl-phosphate(TBP), followed by stripping with water to recover purified phosphoric acid.



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## Description

# METHOD FOR TREATING OF ETCHING ACID WASTE CONTAINING PHOSPHORIC ACID, ACETIC ACID AND NITRIC ACID

### Technical Field

- [1] The present invention relates to a method for treating an acid waste (etching waste) using tri-octyl-phosphate (TOP) and tri-butyl-phosphate (TBP) as extractants and more particularly, a method for separating and recovering acids from an acid waste comprising treating etching waste from the production process of liquid crystals or semiconductors including phosphoric acid, acetic acid and nitric acid with TOP as an extractant to extract acetic acid and nitric acid, treating the raffinate with TBP to extract phosphoric acid with a low purity and purifying phosphoric acid for reuse.

### Background Art

- [2] Generally, the production process of liquid crystals involves many processes such as deposition, resist coating, light exposure, development, etching, resist removal, rinsing and the like. Among them, the etching process uses acid etching solutions comprising acetic acid-nitric acid-phosphoric acid to dissolve aluminum-molybdenum alloy or silver deposited on a glass substrate.
- [3] The acid waste (etching waste) resulting from the use of the etching solution, though varying according to reaction conditions and reaction states of the etching process, comprises 50 to 70wt% of phosphoric acid, 2 to 10wt% of acetic acid and 1 to 10wt% of nitric acid, and other ingredients. Also, the waste solution may contain aluminum metal ions such as aluminum and molybdenum. Therefore, the acid waste is mostly subjected to neutralization process in commissioned agencies without any proper treatment.
- [4] By the neutralization process, phosphate ion ( $\text{PO}_4^{3-}$ ) which forms calcium and hardly soluble salts is removed by inducing neutralization and precipitation calcium carbonate or calcium hydroxide. Acetate ion ( $\text{CH}_3\text{COO}^-$ ) and nitrate ion ( $\text{NO}_3^-$ ) are not removed by neutralization and are, thus, separately treated with activated sludge.
- [5] However, the conventional neutralization treatment has problems of formation of precipitation in a large quantity and treatment of activated sludge, causing increase in treatment cost.
- [6] In addition, the acid recovery method from an acid waste includes membrane separation, ion exchange, solvent extraction and the like.
- [7] The membrane separation method is advantageous in terms of high acid recovery and high acid purity but is disadvantageous in terms of tremendous cost for equipment

investment and complicated operation. The ion exchange method uses an anion exchange resin (Seida and Nakano, 2001) or a calcium zeolite (Takami et al., 2000) to remove acid. However, it has problems in that it is applicable only to treat acid at low concentration, since the exchange capacity is generally small.

[8] The solvent extraction method has advantageous in that it is performed in a closed system continuously and the equipment cost is cheap. Therefore, it is applied to the treatment technology of acid waste from the pickling process of steel, including, for example, "Nisshin process" of Nisshin Steel Co., Ltd. (Yamamoto et al., 1979), "Kawatetsu process" of Kawasaki Steel Corporation (Watanabe et al., 1985), and "AX process" of Sweden (Kuylerstierna and Otteryun, 1974).

[9] However, there has not known a solvent extraction method of tri-component acid waste which can isolate each acid separately for recycle.

[10] Therefore, from the view point of industrial and environmental aspects, the present inventors have conducted research to develop a solvent extraction process of a tri-component acid waste (etching waste) comprising phosphoric acid, acetic acid and nitric acid, which can isolate each acid separately for recycle.

## **Disclosure of Invention**

### **Technical Problem**

[11] Accordingly, the present invention has been made in order to solve the foregoing problems occurring in the prior art, and it is an object of the present invention to provide a method for treating a tricomponent etching waste containing phosphoric acid, acetic acid and nitric acid at a low cost comprising selecting extraction solvents to initially recover acetic acid and nitric acid separately from the waste by extraction/isolation and then recover phosphoric acid through purification and performing separation and recovery of acids at high purity using the extraction solvents.

[12] More particularly, it is an object of the present invention to provide a method for treating an etching waste from the production process of semiconductors or liquid crystals comprising extracting and isolating acetic acid and nitric acid at high purity from the etching waste by solvent extraction, and recovering phosphoric acid at high purity from the raffinate containing phosphoric acid with acetic acid and nitric acid removed.

[13] Thus, it is an object of the present invention to provide a method for treating an etching waste containing phosphoric acid with acetic acid, nitric acid, or a mixture thereof to extract and isolate each acid separately at high purity by using tri-octyl-phosphate (TOP) and tri-butyl-phosphate (TBP) as organic extraction solvents under an optimum condition.

### **Technical Solution**

- [14] To achieve the above object, according to the present invention, there is provided a method for treating an etching waste from the production process of liquid crystals to recover acids from the etching waste by means of solvent extraction comprising: a phase separation process of contacting the etching waste comprising phosphoric acid and acetic acid, nitric acid or a mixture thereof with an organic phase comprising tri-octyl-phosphate (TOP) as an extractant and a diluent at a predetermined concentration ratio, followed by uniformly stirring and standstill to separate an extract phase containing acetic acid, nitric acid or a mixture thereof and raffinate containing phosphoric acid; a separation process of stripping the organic phase containing acetic acid and nitric acid with water to recover acetic acid and nitric acid; and a phosphoric acid recovery process of extracting phosphoric acid from the raffinate with an organic phase comprising tri-butyl-phosphate (TBP) as an extractant and a diluent, followed by stripping with water to recover purified phosphoric acid.

### **Advantageous Effects**

- [15] According to the present invention, it is possible to recover purified phosphoric acid for recycle from countercurrent multi-stages extraction of a tri-component waste solution comprising phosphoric acid and acetic acid, nitric acid or a mixture thereof using tri-octyl-phosphate by selectively separating nitric acid and acetic acid at high purity with TOP in extract phase and recovering phosphoric acid at low purity from raffinate tri-butyl-phosphate, followed by purification.

### **Brief Description of the Drawings**

- [16] Further objects and advantages of the invention can be more fully understood from the following detailed description taken in conjunction with the accompanying drawings in which:
- [17] Fig. 1 shows a McCabe-Thiele diagram and flowchart to determine a theoretical number of extraction stages in extraction of acetic acid from a tricomponent acidic waste solution using tri-octyl-phosphate (TOP) as an extractant in the equilibrium experiment according to the present invention,
- [18] Fig. 2 shows a McCabe-Thiele diagram and flowchart to determine a theoretical number of extraction stages in extraction of nitric acid from tricomponent acidic waste solution using tri-octyl-phosphate (TOP) as an extractant in the equilibrium experiment according to the present invention,
- [19] Fig. 3 shows a McCabe-Thiele diagram and flowchart to determine a theoretical number of stripping stages in stripping of acetic acid from the organic phase containing the extracted acetic acid and nitric acid with water according to the present invention,
- [20] Fig. 4 shows a McCabe-Thiele diagram and flowchart to determine a theoretical number of stripping stages in stripping of nitric acid from the organic phase containing

- the extracted acetic acid and nitric acid with water according to the present invention,
- [21] Fig. 5 shows a McCabe-Thiele diagram and flowchart to determine a theoretical number of extraction stages in extraction of phosphoric acid from the raffinate with acetic acid and nitric acid removed off using tri-butyl-phosphate (TBP) as an extractant;
- [22] Fig. 6 shows a McCabe-Thiele diagram and flowchart to determine a theoretical number of stripping stages in stripping of phosphoric acid from the organic phase containing the extracted phosphoric acid with water according to the present invention, and
- [23] Fig. 7 is a flow chart showing the whole procedures for recovering acids from the tricomponent acid waste using tri-octyl-phosphate and tri-butyl-phosphate.

### **Best Mode for Carrying Out the Invention**

- [24] Now, the present invention is explained in detail as follows. Herein, while the treatment process is described, the repeated explanation on the same construction and operation as the prior art will be omitted. Also, technical terms and scientific terms used herein will have meanings which have been understood by those who have ordinary knowledge in the technical field to which the present invention belongs, unless they are otherwise defined herein.
- [25] The present invention is directed to a method for liquid-liquid extraction to separate nitric acid, acetic acid and phosphoric acid from an etching waste solution from the production process of liquid crystals or semiconductors comprising various acids such as phosphoric acid, nitric acid, acetic acid and the like by using an extractant.
- [26] The extractant which can be used in the present invention comprise tri-octyl-phosphate (TOP) and tri-butyl-phosphate (TBP) diluted in a diluent, in which the extractant are mixed with the diluent at a ratio of 1:0.5 to 1:3. More preferably, tri-octyl-phosphate and tri-butyl-phosphate is diluted in a diluent at a volume ratio of 50%(v/v).
- [27] Here, while not extracting phosphoric acid selectively in solvent extraction and leaving it in raffinate, tri-octyl-phosphate(TOP) extracts nitric acid and acetic acid from the waste solution as the organic phase. Phosphoric acid remaining in the raffinate is extracted by the organic phase of tri-butyl-phosphate organic, followed by purification.
- [28] According to the present invention, the diluent for tri-octyl-phosphate or tri-butyl-phosphate may be alkylbenzene of  $C_8$  to  $C_{14}$ , preferably one selected from the group consisting of Solvesso 150, Solvesso 100, kerosene and a mixture thereof.
- [29] Also, according to the present invention, the extraction process and stripping process are preferably performed by continuous countercurrent multi stages operation.

This is because the cost needed for phase-separation of acetic acid and nitric acid at high purify from the etching waste and recovery of acetic acid and nitric acid from the extract phase is small.

- [30] Meanwhile, in order to determine the number of stages in the continuous counter-current multi stages operation, firstly, an extraction isothermal curve is made by contacting the aqueous phase of the waste solution with the organic phase of the extractant at different phase ratios, following equilibrium, measuring the acid concentration of the extracted phase (organic phase) and the acid concentration of the raffinate phase (aqueous phase) and plotting the data. Then, a stripping isothermal curve which is made by equilibrating the extract phase (organic phase) with water to strip acids, measuring the acid concentration of the aqueous phase and the acid concentration of the organic phase remaining in the extractant and plotting the data. The two curves are applied to the McCabe-Thiele method to theoretically obtain the stage number needed for phase separation process and acid recovery process for optimum extraction and stripping.
- [31] Here, as a result of analyzing Fig. 1 and Fig. 2 made by the McCabe-Thiele method, in case of the phase separation according to the present invention, the waste solution (A) is extracted with tri-octyl-phosphate organic phase (O) at a phase ratio (A/O) 0.4, 96.8% of acetic acid is extracted in 6-stages and 99.2% of nitric acid is extracted in 4-stages while 1.3% of phosphoric acid is extracted (not shown).
- [32] As a result of analyzing Fig. 3 and Fig. 4, in case of the acid recovery process (stripping), when the phase ratio (O/A) of the organic phase (O) and the water (A) is 1.0, 99% acetic acid is extracted in 3 stages and 99.2% of nitric acid is extracted in 2 stages.
- [33] Therefore, in order to optimally strip acetic acid and nitric acid, it is preferably to adjust the phase ratio (A/O) of the aqueous phase (A) of the waste solution and the organic phase (O) containing tri-octyl-phosphate in the extraction process to 0.3 to 0.4 and to adjust the phase ratio (O/A) of the organic phase (O) and water (A) in the stripping process to 0.9 to 1.
- [34] Also, as a result of analyzing Fig. 5 and Fig. 6 made by the McCabe-Thiele method, when the raffinate (A) with the acetic acid and nitric acid removed off is treated with the organic phase (O) containing extracted phosphoric acid, 96% of phosphoric acid is extracted in 4 stages at a phase ratio (A/O) of 1/4(0.25). When the organic phase (O) containing phosphoric acid is stripped with water (A), 99% of phosphoric acid is stripped in 4 stages at a phase ratio (O/A) of organic phase (O) and water (A) of 2 to give phosphoric acid at high purity.
- [35] Therefore, in order to purify phosphoric acid from the raffinate after the phase separation process, it is preferably to adjust the phase ratio (A/O) of the raffinate (A)

and the organic phase (O) containing tri-octyl-phosphate to 0.1 to 0.4 and to adjust the phase ratio (O/A) of the organic phase (O) containing the extracted phosphoric acid and water (A) to 1 to 3.

[36] Also, according to the present invention, the etching waste may be the one that is generated in the production process of liquid crystals or semiconductors and satisfy the above-described etching waste requirements.

[37] Further, according to the present invention, in addition to preparation of purified phosphoric acid at high purity, it is possible to prepare raffinate containing phosphoric acid at low purity with a small amount of aluminum and molybdenum, which can be used in production of chemical fertilizer without processing, through the separation and recovery processes of acetic acid and nitric acid, since the etching waste from the production process of liquid crystals contains a small amount of aluminum and molybdenum.

[38] Now, the present invention is explained in further detail using the following examples. However, it should be understood that the examples are intended to concretely illustrate the present invention and the present invention is not limited thereto.

[39]

[40] [Example 1] extraction and stripping of acetic acid and nitric acid by TOP in mock waste solution

[41] 1. Extraction isothermic curve and stripping isothermic curve

[42] In this Example, an equilibrium experiment was performed to make extraction isothermic curve and stripping isothermic curve to determine conditions for optimum extractant concentration and the number of extraction and stripping stages.

[43] In the equilibrium experiment, the extraction was performed by mixing the aqueous phase of the waste solution comprising phosphoric acid and acetic acid, nitric acid or a mixture thereof with the organic phase (O) containing an extractant at a phase ratio (A/O) of 0.1 to 10, followed by stirring. Once the mixture reached equilibrium state where further mass transfer was not observed, the aqueous phase and the organic phase were separated using a separatory funnel and the acid concentration of the aqueous phase and the acid concentration of the organic phase were measured at different phase ratios. By using the measured data, the extraction isothermic curve as shown in Fig. 1 was made.

[44] Also, the stripping experiment was performed by mixing the organic phase containing the extract and water at a phase ratio (O/A) of 0.1 to 10, followed by stirring. In the equilibrium state as in the extraction method, the acid concentration of the organic phase remaining in the extractant and the acid concentration of the aqueous phase stripped to water were measured. By using the measured data, the stripping

isothermic curve as shown in Fig. 2 was made.

[45] Here, the extractant comprised 50%(v/v) tri-octyl-phosphate (Wako Pure Chemicals Industries, Ltd., Japan) diluted in 50%(v/v) Solvesso 150 (Toei Corporation, Japan) and the tripping agent was water (distilled water).

[46] The mock waste solution was combined according to the concentrations listed in Table 1 below under a proper condition.

[47] Table 1

| acetic acid ( $\text{CH}_3\text{COOH}$ ) | nitric acid ( $\text{HNO}_3$ ) | phosphoric acid ( $\text{H}_3\text{PO}_4$ ) |
|------------------------------------------|--------------------------------|---------------------------------------------|
| 0.8M/L                                   | 0.35M/L                        | 5.0M/L                                      |

[48] As a result, from the extraction isothermic curve, it was proved that tri-octyl-phosphate used as an extractant extracted nitric acid and acetic acid simultaneously. With respect to the extraction capacity of tri-octyl-phosphate (TOP) in tri-component acid system, nitric acid was higher than acetic acid, since the concentration of nitric acid in the organic phase was higher than that of acetic acid. Meanwhile, it was found that little of phosphoric acid was extracted (Fig. 1 and Fig. 2).

[49] In the stripping experiment using water (distilled water), it was shown that nitric acid was more likely stripped than nitric acid (Fig. 3 and Fig. 4).

[50] 2. Determination of theoretical stage number of countercurrent multi stages operation

[51] McCabe-Thiele diagrams were made by combining the extraction isothermic curve and the stripping isothermic curve of Example 1-1 with processing lines (operating lines: A/O phase ratio) to determine theoretical number of stages needed for extraction and stripping.

[52] Firstly, the etching waste (A) combined according to Table 1 was mixed with tri-octyl-phosphate extractant (O) of Example 1-1 at a phase ratio (A/O) of 0.1 to 10, followed by equilibrium. Then, the acid concentrations of the extract phase containing acetic acid and nitric acid were measured and the result is shown in an extraction isothermic curve (Fig. 1 and Fig. 2).

[53] Also, the extract phase (O) was mixed with water (A) at a ratio (O/A) of 0.1 to 10, followed by equilibrium. Then, the acid concentrations of the recovered acetic acid and nitric acid were measured and the result is shown in a stripping isothermic curve (Fig. 3 and Fig. 4).

[54] The extraction isothermic curve and the stripping isothermic curve were combined with processing lines (operating lines: A/O phase ratio) by drawing successive vertical and horizontal lines and the result is shown in Fig. 1.

[55] As shown in the extraction isothermic curve in Fig. 1, when the initial concentration of acetic acid in the waste solution was 0.8M/L and the phase ratio (A/O) of waste

solution and organic extraction solvent was 0.4, 97% of acetic acid was extracted in 6 stages with the organic phase. Thus, the concentration of acetic acid in the organic phase contained was 0.31M/L and the concentration of acetic acid remaining in the raffinate was 0.256M/L. Also, from the result shown in Fig. 2, it was found that when the initial concentration was 0.35M/L and the phase ratio was 0.4, 99.0% of nitric acid was extracted in 2 stages, indicating that the nitric acid concentration of the organic phase was 0.138M/L.

[56] Also, as shown in the stripping isothermic curve in Fig. 3, when the initial concentration of acetic acid in the extract phase (organic phase) was 0.31M/L and the phase ratio (A/O) was 1, 99% of acetic acid was theoretically stripped in 3 stages with the water (aqueous phase). From the result shown in Fig. 4, it was found that when the initial concentration was 0.138M/L and O/A was 1, 99.2% of nitric acid was theoretically recovered in 2 stages, indicating that nitric acid was recovered at a concentration of 0.137M/L.

[57] As a result of the treatment process of the waste solution to extract acetic acid and nitric acid from the waste solution while leaving phosphoric acid in the raffinate by the equilibrium experiment, it was analyzed that the 6-stages extraction process at a phase ratio (A/O) of 0.4 and the 3-stages stripping process at a phase ratio (O/A) of 1.0 could produce effectively 95.8% of acetic acid and 98.2% of nitric acid.

[58]

[59] [Example 2] Purification of phosphoric acid by TBP

[60] 1. Construction of extraction isothermic curve and stripping isothermic curve

[61] The raffinate resulting the extraction of acetic acid and nitric acid from the mixed acid waste by tri-octyl-phosphate may contain phosphoric acid and a small amount of metal ingredients. This example was performed to extract and separate those substances by TBP using a mock waste solution containing phosphoric acid at 5.0M/L.

[62] Fig. 5 is a McCabe-Thiele diagram showing the result of the extraction experiment of phosphoric acid at various concentrations with 50% tri-butyl-phosphate (TBP) at 25°C by plotting an isothermic curve and combining the curve with operating lines.

[63] By drawing horizontal and vertical lines as shown in Fig. 5, it was found that when the initial concentration of phosphoric acid in the aqueous solution (A) was 5.0M/L and the phase ratio (O/A) was 1/4, 96% of phosphoric acid was extracted in 4 stages with the organic phase by 50% tri-butyl-phosphate and the concentration of phosphoric acid in the organic phase was about 1.2M/L. At this moment, the concentration of phosphoric acid in the raffinate was about 0.2M/L.

[64] After extraction, phosphoric acid in the organic phase was subjected to the stripping process using water (distilled water) for purification of phosphoric acid. The stripping isothermic curve of this stripping process was combined with operating lines and the

result is shown in Fig. 6.

[65] By drawing horizontal and vertical lines as shown in Fig. 6, it was found that when the initial concentration of phosphoric acid in the extract phase (O) was 1.2M/L and the phase ratio (O/A) of the extract phase (O) to water (A) was 2, 99% of phosphoric acid was theoretically striped in 4 stages with water (aqueous phase).

[66] As a result of this experiment to recover purified phosphoric acid from the waste solution by 50% tri-butyl-phosphate (TBP), it was analyzed that the 4-stages extraction process at a phase ratio (A/O) of 1/4(0.25) and the 4-stages stripping process at a phase ratio (O/A) of 2.0 could produce effectively 95% of phosphoric acid.

### **Industrial Applicability**

[67] As described above, according to the present invention, it is possible to recover purified phosphoric acid for recycle from countercurrent multi-stages extraction of a tri-component waste solution comprising phosphoric acid and acetic acid, nitric acid or a mixture thereof using tri-octyl-phosphate by selectively separating nitric acid and acetic acid at high purity with TOP in extract phase and recovering phosphoric acid at low purity from raffinate tri-butyl-phosphate, followed by purification.

[68] Meanwhile, the etching waste discharged from the production process of liquid crystals may contain a small amount of aluminum and molybdenum. However, through the separation and recovery processes according to the present invention, it is possible to separate aluminum and molybdenum from the raffinate and recovery phosphoric acid a high purity, which can be recycled to the production of etching solution or used in other applications.

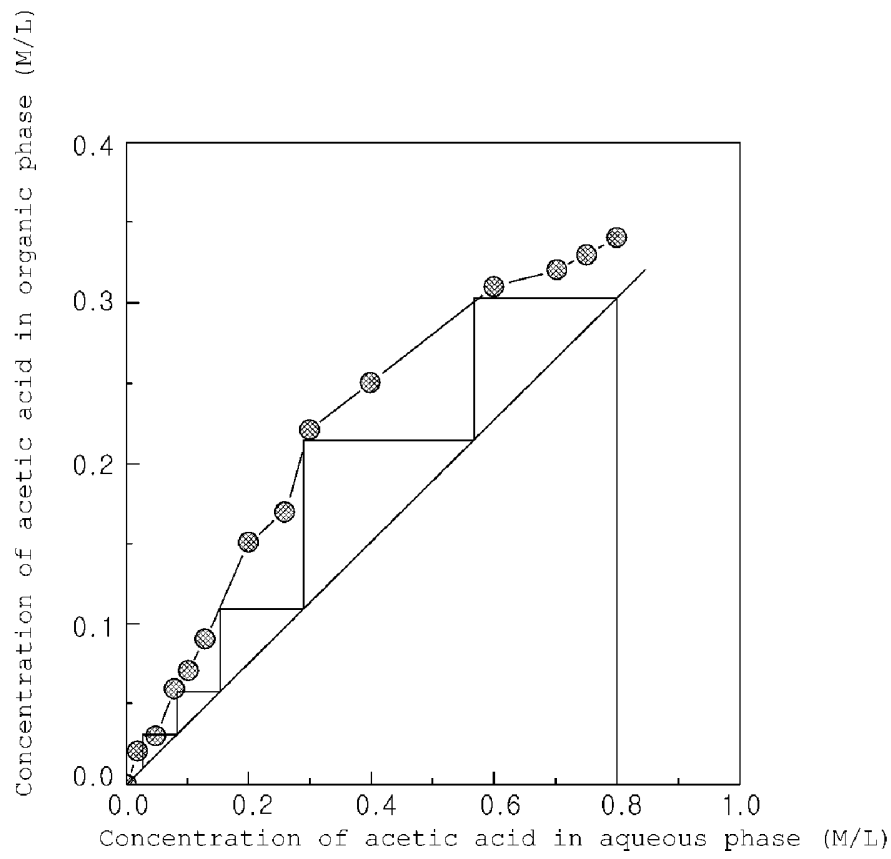
[69] Also, according to the acid separation and recovery method according to the present invention, it is possible to substitute the conventional neutralization method which requires high treatment cost, reducing the process cost.

[70]

## Claims

- [1] A method for treating an etching waste to recover acids from the etching waste by means of solvent extraction comprising:  
a phase separation process of contacting the etching waste comprising phosphoric acid and acetic acid, nitric acid or a mixture thereof with an organic phase comprising tri-octyl-phosphate (TOP) as an extractant and a diluent at a predetermined concentration ratio, followed by uniformly stirring and standstill to separate an extract phase containing acetic acid, nitric acid or a mixture thereof and raffinate containing phosphoric acid;  
a separation process of stripping the organic phase containing the extracted acetic acid and nitric acid with water to recover acetic acid and nitric acid; and  
a phosphoric acid recovery process of extracting phosphoric acid from the raffinate with an organic phase comprising tri-butyl-phosphate(TBP) as an extractant and a diluent, followed by stripping with water to recover purified phosphoric acid.
- [2] The method according to claim 1, in which the organic phase in the phase separation process comprises tri-octyl-phosphate (TOP) as an extractant and a diluent selected from the group consisting of Solvesso 150, Solvesso 100, kerosene and a mixture thereof in a ratio of 1:0.5 to 1:3.
- [3] The method according to claim 1, in which the organic phase in the acid recovery process comprises tri-butyl-phosphate (TBP) as an extractant and a diluent selected from the group consisting of Solvesso 150, Solvesso 100, kerosene and a mixture thereof in a ratio of 1:0.5 to 1:3.
- [4] The method according to claim 1, in which the phase separation process is performed at a phase ratio (A/O) of the waste solution (A) and the organic phase (O) containing tri-octyl-phosphate of 0.2 to 0.5.
- [5] The method according to claim 1, in which the stripping of acetic acid and nitric acid from the organic phase containing the extracted acetic acid and nitric acid is performed at a phase ratio (O/A) of the organic phase (O) and water (A) of 0.9 to 1.
- [6] The method according to claim 1, in which the phosphoric acid extraction process is performed at a phase ratio (A/O) of the raffinate (A) and the organic phase (O) containing tri-butyl-phosphate of 0.1 to 0.4.
- [7] The method according to claim 1, in which the stripping process of phosphoric acid is performed at a phase ratio (O/A) of the organic phase (O) containing the extracted phosphoric acid and water (A) of 1 to 3.

[Fig. 1]



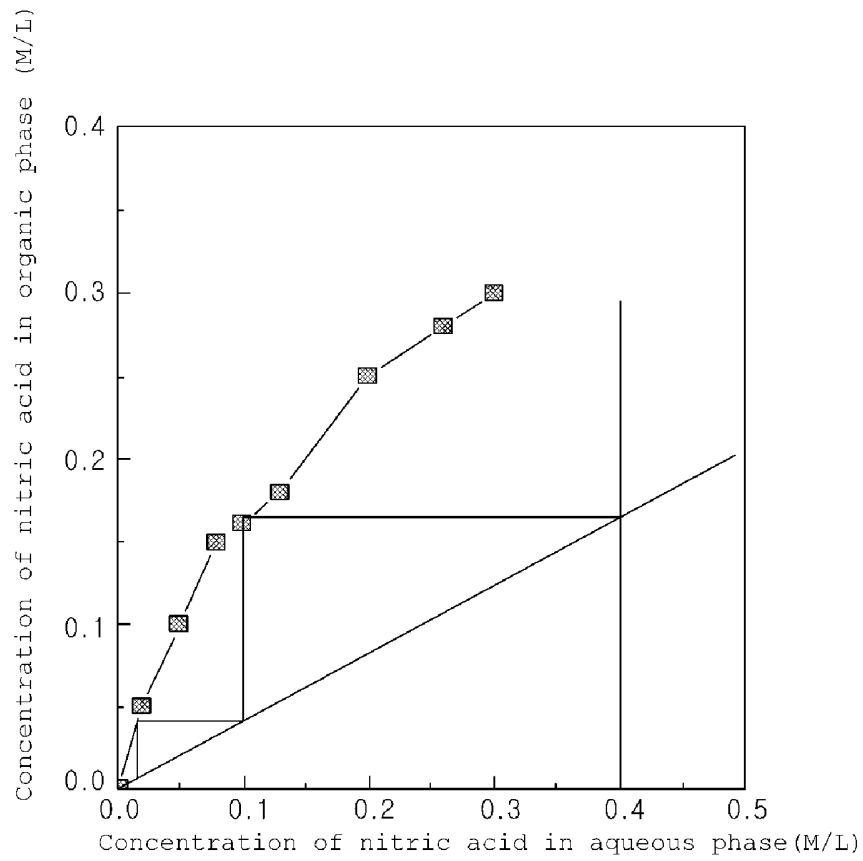
0.31 M/L Acetic acid  
(Organic phase)

50% TOP ..... A/O=0.4, 6-stages extraction .....  
 Recovery rate of acetic acid: 96.8%

0.025 M/L Acetic acid  
(Raffinate phase)

0.8 M/L Acetic acid  
(Aqueous phase)

[Fig. 2]



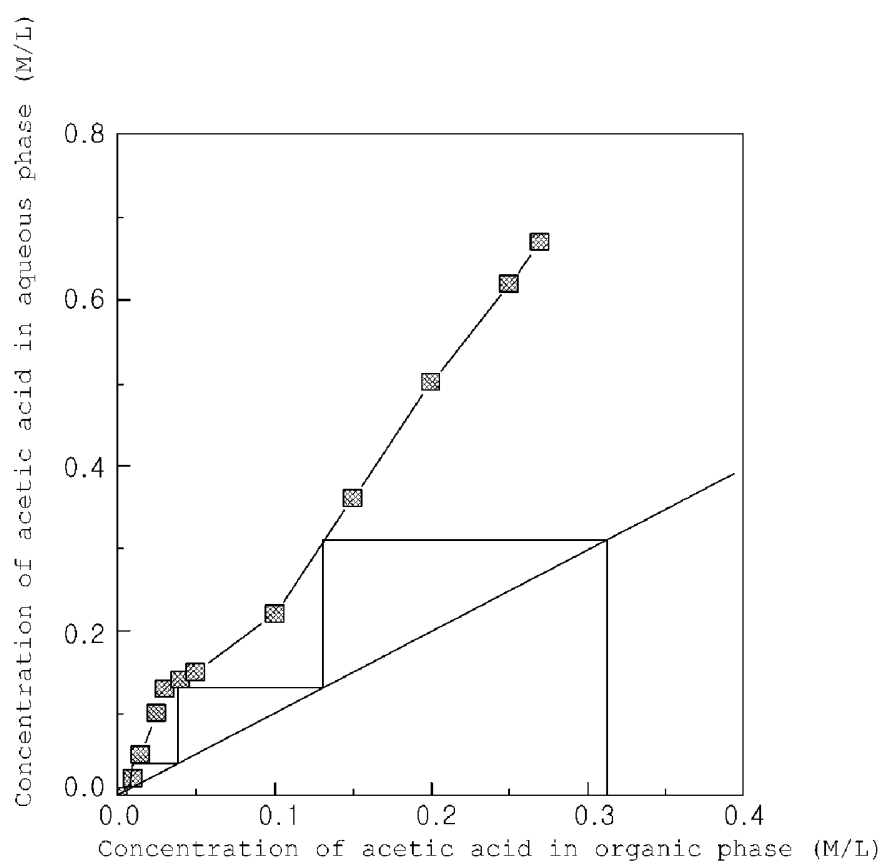
0.138 M/L Nitric acid  
(Organic phase)

50% TOP ..... → A/O=0.4, 2-stages extraction  
← Recovery rate of nitric acid:99% ←

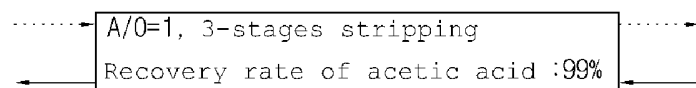
0.025 M/L Nitric acid  
(Raffinate phase)

0.8 M/L Nitric acid  
(Aqueous phase)

[Fig. 3]

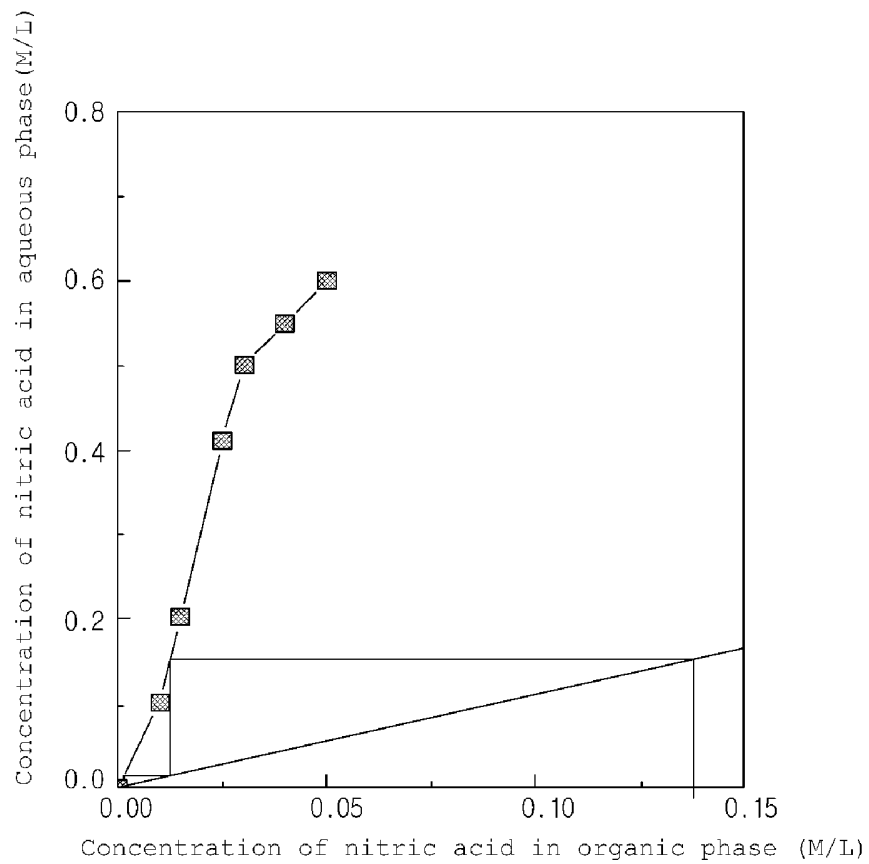


0.31 M/L Acetic acid

Removal of organic  
phase0.307 M/L Acetic acid  
(Aqueous stripping  
solution phase)

Water (Aqueous phase)

[Fig. 4]



0.138 M/L Nitric acid

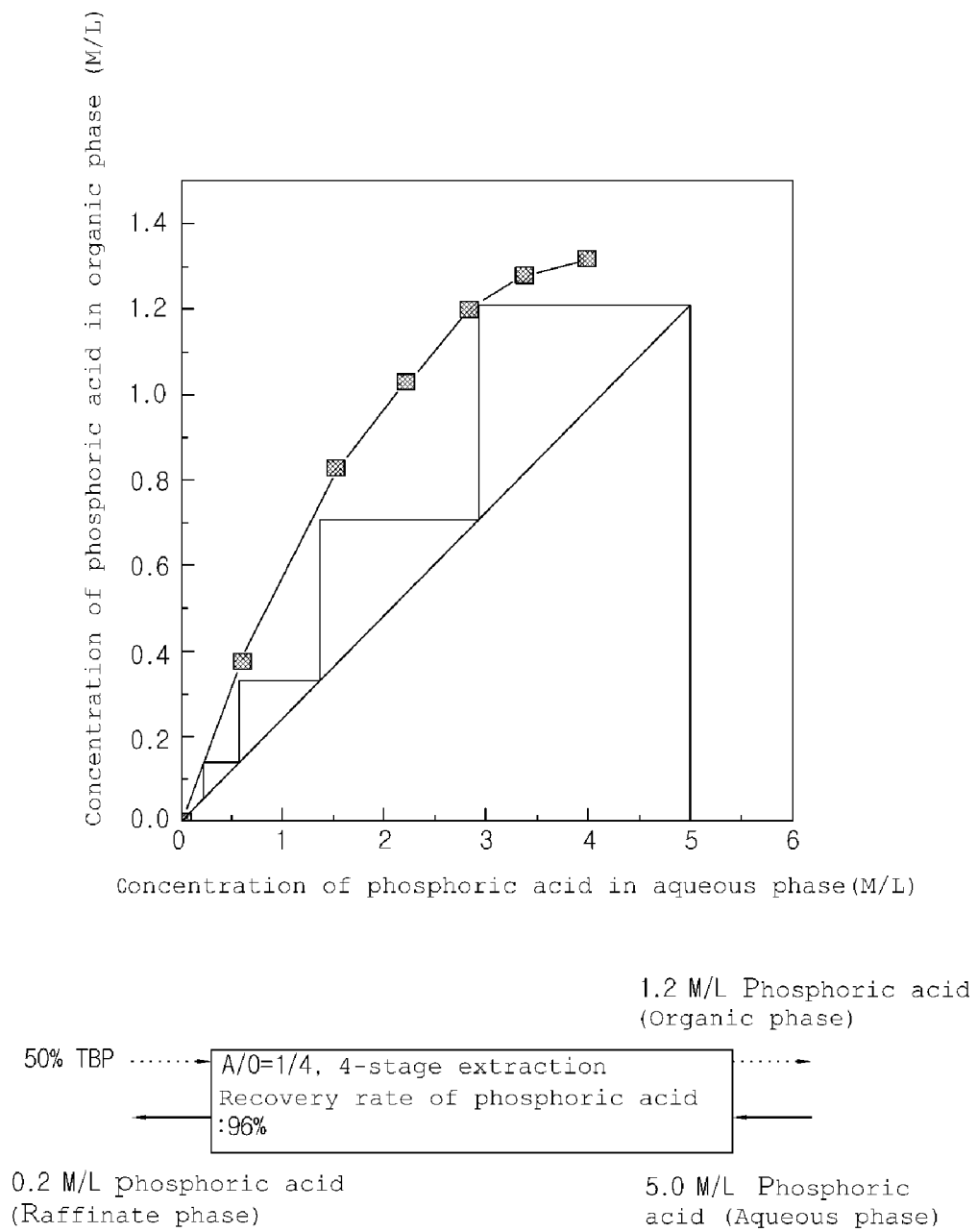
Removal of organic  
phase

.....→ A/O=1, 2-stages stripping  
 Recovery rate of nitric acid :99.2% ←.....

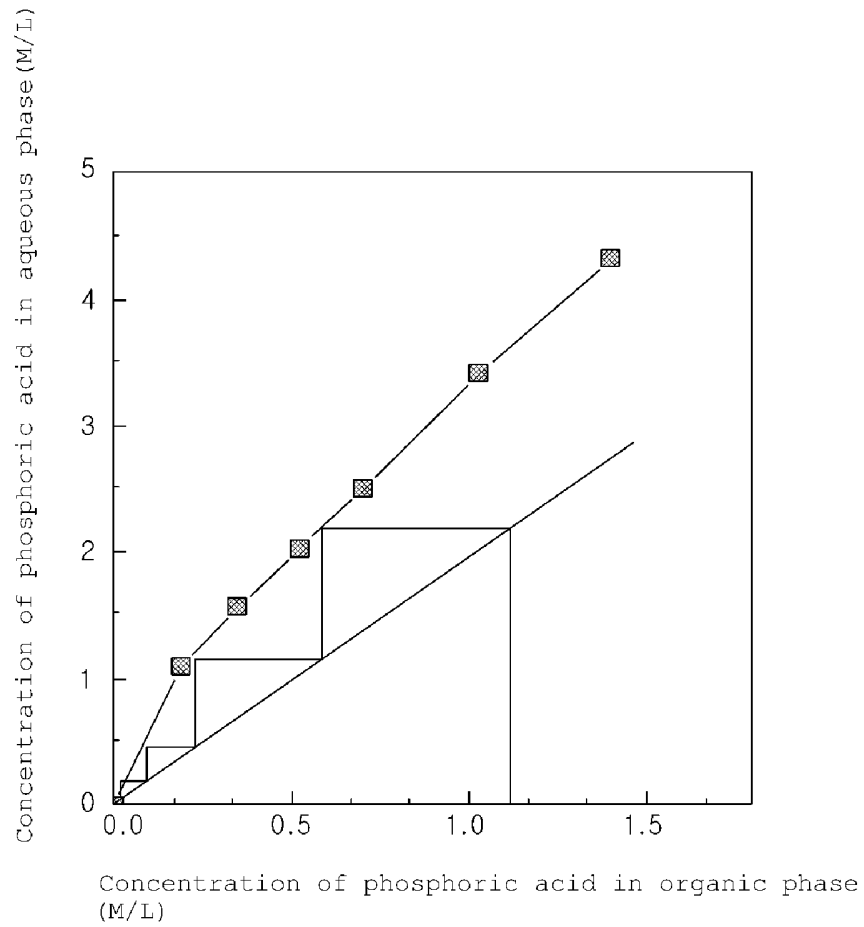
0.137 M/L Nitric acid  
 (Aqueous stripping  
 solution phase)

Water (Aqueous phase)

[Fig. 5]

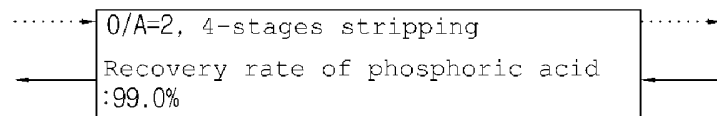


[Fig. 6]



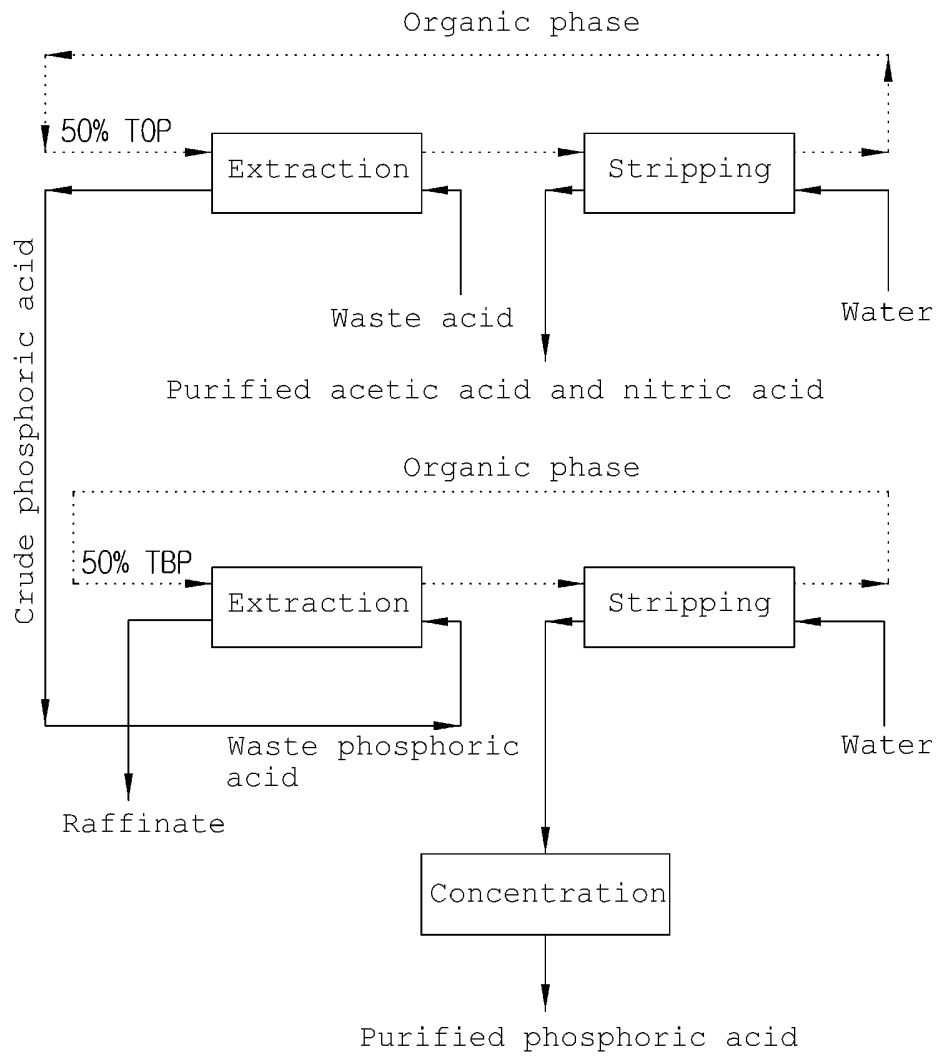
1.2 M/L Phosphoric acid

Removal of organic phase

1.19 M/L Phosphoric acid  
(Aqueous stripping  
solution phase)

Water (Aqueous phase)

[Fig. 7]



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR2005/001665

**A. CLASSIFICATION OF SUBJECT MATTER****IPC7 B01D 11/04**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

B01D, C25B, C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Korean Patents and applications for inventions for since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
eKIPASS

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages           | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------|-----------------------|
| A         | US 4177119 A (SOLEX RESEARCH CORP.) 4 DECEMBER 1979<br>See abstract, claim 1 and claim 6     | 1                     |
| A         | KR 1999-7705 A (JAE WOO, AHN) 25 JANUARY 1999<br>See abstract and figure 1                   | 1                     |
| A         | KR 1998-40479 A (DEOK KI, AHN ET AL.) 17 AUGUST 1998<br>See abstract and claim 1             | 1                     |
| A         | JP 55-90423 A (TOAGOSEI CHEMICAL INDUSTRY CO., LTD.) 9 JULY 1980<br>See abstract and claim 1 | 1                     |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

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"E" earlier application or patent but published on or after the international filing date

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

12 SEPTEMBER 2005 (12.09.2005)

Date of mailing of the international search report

**12 SEPTEMBER 2005 (12.09.2005)**

Name and mailing address of the ISA/KR



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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

PCT/KR2005/001665

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                       | Publication<br>date                                                     |
|-------------------------------------------|---------------------|----------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| US 4177119 A                              | 04.12.1979.         | IT 1084025 A<br>FR 2343695 A1<br>JP 52108396 A2<br>DE 2710328 A1<br>SE 7702585 A | 25.05.1985.<br>07.10.1977.<br>10.09.1977.<br>15.09.1977.<br>10.09.1977. |
| KR 1999-7705 A                            | 25.01.1999.         | None                                                                             |                                                                         |
| KR 1998-40479 A                           | 17.08.1998.         | None                                                                             |                                                                         |
| JP 55-90423 A                             | 09.07.1980.         | None                                                                             |                                                                         |