

METHOD AND APPARATUS FOR OBTAINING PURIFIED PHOSPHORIC ACID FROM PHOSPHORIC ACID AQUEOUS SOLUTION CONTAINING PLURAL METAL IONS

INCORPORATION BY REFERENCE

The disclosure of Japanese Patent Application No. 2007-028820 filed on February 8, 2007 including the specification, drawings and abstract is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001]

Though a mixed aqueous solution of nitric acid - acetic acid - phosphoric acid (hereinafter, referred to as "mixed acid aqueous solution") used in a metal etching process is discharged as a waste liquid containing a plurality of metal ions in a concentration more than an upper limit (usually, 500 to 1000 ppm based on the weight) used for etching, the present invention relates to a method and apparatus for removing metal ions from such a mixed acid aqueous solution containing the metal ions (hereinafter, referred to as "mixed acid aqueous solution waste liquid") to obtain a purified phosphoric acid. Particularly, the present invention relates to a method and apparatus suitable for treating a phosphoric acid aqueous solution containing metal ions in a high concentration (from 500 ppm based on the weight to an upper limit concentration in which a metal can be dissolved as a metal ion in a phosphoric acid aqueous solution) which is a residual phosphoric acid aqueous solution (which is subjected to a disposal as it is, at present) obtained after a primary treatment by a melt crystallization method or a solvent extraction method.

2. Description of the Related Art

[0002]

In a metal etching process such as A1 in a semiconductor producing factory or in a liquid crystal display production, as a new fresh liquid of a mixed acid aqueous solution, for example a mixture of phosphoric acid, nitric acid, acetic acid and water is used and a total metal ion concentration in such a solution is 100 ppb or less. However, in such a mixed acid aqueous solution, according to the use thereof, the dissolution of a metal is

progressed and consequently, not only the metal ion concentration is elevated, but also the composition of the solution is changed due to an evaporation or an attaching to a material to be etched of volatile substances (such as nitric acid, acetic acid, water), so that the etching ability of the solution is lowered. Therefore, conventionally, by exchanging a part or the whole of the solution with a new fresh liquid, not only the total metal ion concentration is suppressed low (around 500 to 1000 ppm or less based on the weight), but also the change of the composition is also suppressed to maintain the etching ability. However, conventionally, a mixed acid aqueous solution waste liquid containing a plurality of metal ions discharged from a metal etching process was subjected to a disposal, because with such a mixed acid aqueous solution, the etching ability is lowered according to an elevation of the metal concentration in the solution. Thus, a treating apparatus for removing metal ions from a mixed acid aqueous solution waste liquid discharged after the use thereof as an etching solution and for recovering a mixed acid aqueous solution in a high yield, is required.

A first step for purifying a mixed acid aqueous solution waste liquid discharged from an A1 metal etching apparatus is evaporating and separating volatile substances (nitric acid, acetic acid, most of water) by an evaporation or distillation method. Since phosphoric acid and metal ions both are a nonvolatile substance, so that they cannot be separated by the evaporation or distillation. In this step, phosphoric acid (hereinafter, referred to as "concentrated phosphoric acid") has a concentration of about 90% by mass and contains about 10% by mass of water.

[0003]

As a general method for separating metal ions present in a solution, there can be mentioned an ion-exchanging resin method, a diffusion dialysis method, a diaphragm electrodialysis method and an adsorption method using an activated carbon. However, even when these methods are applied to a mixed acid aqueous solution waste liquid or concentrated phosphoric acid, since phosphoric acid having a high concentration is highly corrosive, the waste liquid contains both anions and cations as metal ions and the following problems are caused, metal ions cannot be satisfactorily separated.

In the ion-exchanging resin method, metal ions dissolved in a high concentrated acid can be hardly ion-exchanged. Also, it was found that a reproducing efficiency of a resin is low. In the diffusion dialysis method, obtained phosphoric acid is diluted and a large quantity of a dialysis residual liquid is generated. In the diaphragm electrodialysis method, a disadvantage is caused wherein NO_x is generated by the oxidation of nitric acid

in a mixed acid aqueous solution waste liquid. In the electrodialysis, since a phosphoric acid ion has a similar ion radius to that of a molybdic acid ion and has the same moving rate as that of a molybdic acid ion, the two cannot be separated from each other. In the adsorption method using an activated carbon, a mixed acid aqueous solution waste liquid is colored by an activated carbon.

[0004]

On the other hand, as one of purification methods of concentrated phosphoric acid, there can be mentioned a metal extracting agent method (Japanese Patent Application No. JP2005-142444). However, by this method, though the amount of Mo could be reduced, the amount of Al could not be effectively reduced. Further, when in concentrated phosphoric acid, as a metal ion, both a cation (Al^{3+}) and an anion (in the form of an oxidized metal, such as MoO_4^{2-}) are dissolved, for reducing the amounts of both the two ions, 2 sets of an extraction tower and reverse extraction tower are necessary for cations and for anions, so that not only a lot of equipment cost is necessary, but also an operating cost is expected to be elevated and consequently, it becomes difficult to utilize the merit for the reuse of phosphoric acid.

As other purification methods of a concentrated phosphoric acid solution, a crystallization method (Japanese Patent Application No. JP2004-255388 and Japanese Patent No. 3382561) is shown. However, this method is a batch-wise treating method and there is such a problem that a fine temperature control is necessary and the treating time is long.

Further, generally known as a purification method is a technology of a continuous crystallization method (*Zouhoshouseki (Enlarged Crystallization)* p. 73 to 82, enlarged in 25th December, 1983, published by Kagaku Kogyosha Co., Ltd). However, when this method is applied to concentrated phosphoric acid, since a purification purity of a phosphoric acid hemihydrate crystal depends on a metal concentration in a mother liquor, the yield thereof has an upper limit of around 80% by mass and in terms of effective utilization of the resource, it is desired to further enhance the yield.

[0005]

On the other hand, with respect to the coprecipitation related to the present invention, on the page 74 of "*Teiryoubunsekikagaku (Quantitative analytic chemistry)*" (revised 17th edition) (original author: R.A. Day and Jr.A.L. Underwood; published by Baifukan Co., Ltd., 1992), the followings are described.

"The coprecipitation means a phenomenon in which when a sediment is precipitated,

soluble substances are also precipitated accompanying the sediment. The coprecipitation phenomenon is caused sometimes by a generation of a mixed crystal, or sometimes due to the adsorption of ions to the sediment during the precipitate formation. In the case of the former, impurities enter actually into a crystal lattice of the precipitate. In the case of the later, adsorbed ions are dragged with the sediment during a pseudo-precipitation to be precipitated together with the sediment."

However, this literature explains only a general coprecipitation phenomenon and there is no description with respect to the coprecipitation of metal ions in concentrated phosphoric acid according to the present invention at all.

SUMMARY OF THE INVENTION

[0007]

Thus, under the above-noted background, the present invention has been contemplated and the objects of the present invention are to provide a method and apparatus for obtaining purified phosphoric acid by separating and removing metal ions from a phosphoric acid solution containing a plurality of metal ions, and further, to provide a system for reusing the recovered purified phosphoric acid by applying the system to a mixed acid aqueous solution waste liquid containing phosphoric acid in a high concentration discharged from a metal etching process.

[0008]

The above-noted problems are solved by the following aspects according to listed 1) through 8).

1) According to a first aspect of the present invention, a method for obtaining purified phosphoric acid including:

[1] crystallizing and coprecipitating that separate out an inorganic salt crystal from a phosphoric acid aqueous solution containing a plurality of metal ions and coprecipitate metal ions including:

(a) mixing a phosphoric acid aqueous solution containing a plurality of metal ions with an inorganic salt aqueous solution;

(b) separating out an inorganic salt crystal and coprecipitating simultaneously the metal ions by further mixing an organic poor solvent which is soluble in phosphoric acid and does not dissolve an inorganic salt with the above resultant mixture; and

(c) solid-liquid separating by filtering the inorganic salt crystal containing the metal ions; and

[2] evaporating that obtains purified phosphoric acid by evaporating an organic poor solvent and water in a filtrate obtained by the filtration,

wherein the amount of metal ions dissolved in the phosphoric acid / organic poor solvent mixture in the separating out is less than the amount of metal ions in the phosphoric acid solution used in the mixing.

2) According to a second aspect, the method for obtaining purified phosphoric acid according to the first aspect, wherein the crystallizing and coprecipitating and the evaporating are repeated further in plural times with respect to the purified phosphoric acid obtained by the method according to the first aspect to obtain purified phosphoric acid having a higher concentration.

3) According to a third aspect, the method for obtaining purified phosphoric acid according to any one of the first and second aspects, wherein the phosphoric acid aqueous solution containing a plurality of metal ions contains metal ions in a concentration of from 500 ppm based on the weight to an upper limit concentration in which a metal can be dissolved as a metal ion in the phosphoric acid aqueous solution.

4) According to a fourth aspect, the method for obtaining purified phosphoric acid according to any one of the first to third aspects, wherein the inorganic salt crystal containing metal ions obtained in the crystallizing and coprecipitating is dissolved in water; the inorganic salt crystal is separated out by cooling to separate a coprecipitated metal from the inorganic salt; the inorganic salt is filtered to be recovered; from the recovered inorganic salt, an aqueous solution of the inorganic salt is prepared; and the prepared inorganic salt aqueous solution is reused in the mixing according to the first aspect.

5) According to a fifth aspect, a purified phosphoric acid manufacturing apparatus for performing the method according to any one of the first to third aspects including at least:

an inorganic salt dissolving vessel for dissolving an inorganic salt to prepare an inorganic salt aqueous solution;

a crystallizing and coprecipitating vessel equipped with a stirrer for mixing a phosphoric acid aqueous solution containing a plurality of metal ions and an organic poor solvent with the inorganic salt aqueous solution and to separate out a crystal of the

inorganic salt and to coprecipitate simultaneously the metal ions;

a filtering apparatus for filtering the obtained inorganic salt crystal containing the metal ions to separate solid-liquid; and

an organic solvent evaporating apparatus equipped with a heating unit for evaporating the organic poor solvent and water from the resultant filtrate.

6) According to a sixth aspect, the purified phosphoric acid manufacturing apparatus according to the fifth aspect, further including:

an inorganic salt crystallizing and purifying vessel for dissolving the inorganic salt crystal containing the metal ions filtered by the filtering apparatus in warm water and for separating out again the inorganic salt crystal by cooling; and

a filtering apparatus for separating the inorganic salt crystal separated out in the inorganic salt crystallizing and purifying vessel.

7) According to a seventh aspect, a method for reusing an etching liquid including:

recovering an used mixed acid aqueous solution waste liquid containing a plurality of metal ions generated in a metal etching process using a mixed acid aqueous solution composed of phosphoric acid, nitric acid, acetic acid and water;

evaporating that fractionally-distills the mixed acid aqueous solution waste liquid by evaporating nitric acid, acetic acid and most of water from the mixed acid aqueous solution waste liquid into a distillate containing nitric acid, acetic acid and water and concentrated phosphoric acid containing phosphoric acid and a plurality of metal ions;

purificating that obtains purified phosphoric acid by coprecipitating and separating the metal ions in the concentrated phosphoric acid using the apparatus according to the fifth or sixth aspect; and

concentration controlling that controls a liquid concentration by adding the distillate to the obtained purified phosphoric acid to prepare a recycled mixed acid aqueous solution and uses the recycled mixed acid aqueous solution again in the metal etching.

8) According to an eighth aspect, the method for reusing an etching liquid according to the seventh aspect, further including a separating out that includes:

separating out a phosphoric acid hemihydrate crystal from the concentrated phosphoric acid obtained in the evaporating using a melt crystallizing apparatus;

solid-liquid separating the phosphoric acid hemihydrate crystal using a filtering

apparatus;

transferring the obtained phosphoric acid hemihydrate crystal into the concentration controlling; and

transferring the filtrate obtained from the solid-liquid separation in which metal ions are concentrated into the crystallizing and coprecipitating vessel according to the fifth or sixth aspect.

[0009]

According to the present invention, a method and apparatus for obtaining purified phosphoric acid by easily removing metal ions from a phosphoric acid aqueous solution containing a plurality of metal ions can be provided, and further, by applying the method and apparatus to a mixed acid aqueous solution waste liquid containing a high concentration of phosphoric acid discharged from a metal etching process, a system for reusing a recovered purified phosphoric acid can be provided.

Further, by incorporating an apparatus for obtaining purified phosphoric acid according to the present invention in an online of a metal etching apparatus, a concentration of metal ions in a mixed acid aqueous solution tank can be always maintained at a certain value or less and not only an etching process is stabilized, but also a supplementing amount of a mixed acid aqueous solution new fresh liquid can be largely reduced (10% by mass or less of that in a conventional apparatus).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view showing an apparatus for a metal etching process;

FIG. 2 is a schematic view showing an evaporating apparatus as a part of a mixed acid aqueous solution purifying apparatus;

FIG. 3 is a schematic view showing one example of a metal etching liquid recycling system;

FIG. 4 is a flow chart showing a material balance per each fundamental block in Example 3;

FIG. 5 is a schematic view showing another example of a metal etching liquid recycling system;

FIG. 6 is a flow chart showing a material balance per each fundamental block in Example 5; and

FIG. 7 is a schematic view showing a mechanism of the coprecipitation according to some aspects of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010]

Hereinafter, the above-described present invention is described more specifically.

The present inventors have made extensive and intensive studies and as a result, a method and apparatus for removing and separating metal ions to obtain purified phosphoric acid by applying a crystallization and coprecipitation phenomenon particularly effective to a phosphoric acid aqueous solution containing metal ions in a high concentration (from 500 ppm based on the weight to an upper limit concentration in which a metal can be dissolved as a metal ion in a phosphoric acid aqueous solution) was found, and further, it was also found that by applying the method and apparatus to concentrated phosphoric acid containing a plurality of metal ions in a metal etching process, phosphoric acid can be recovered in a high yield and reused. Here, purified phosphoric acid according to an embodiment of the present invention means phosphoric acid from which metal ions have been separated and removed and which has a concentration of phosphoric acid of around 90% by mass.

The method of an embodiment of the present invention includes the following principle. By distilling off nitric acid, acetic acid and most of water from a mixed acid aqueous solution waste liquid containing a plurality of metal ions after used in an etching, concentrated phosphoric acid is obtained and to the obtained concentrated phosphoric acid, an inorganic salt is added. At this time, since an inorganic salt has generally such properties as to be easily dissolved in water and to be hardly dissolved in an organic solvent or concentrated phosphoric acid, a part of the inorganic salt is dissolved in a small amount of water in concentrated phosphoric acid. However, other excessive inorganic salts are not dissolved in the water. When to such concentrated phosphoric acid, an organic poor solvent is added, the inorganic salts dissolved in the concentrated phosphoric acid are crystallized and accompanying the crystallization of the inorganic salts, metal ions dissolved in the concentrated phosphoric acid are precipitated. This phenomenon is the coprecipitation according to an embodiment of the present invention. Thereafter, by filtering a suspension obtained by the cause of a crystallization and a coprecipitation, the suspension is solid-liquid separated into a solid content composed of an inorganic salt crystal and metal ions dissolved in the concentrated phosphoric acid and a liquid content composed of an organic poor solvent and a phosphoric acid aqueous solution. Further, by distilling the obtained filtrate, an organic poor solvent and a phosphoric acid aqueous

solution are fractionally-distilled to obtain purified phosphoric acid. FIG. 7 shows a mechanism of the coprecipitation according to an embodiment of the present invention.

In an embodiment of the present invention, a mixed acid aqueous solution waste liquid containing a plurality of metal ions after used in the etching is concentrated and to the obtained concentrated phosphoric acid, an inorganic salt is added. However, when the concentration of the phosphoric acid aqueous solution in the pretreating process is unsatisfactory, a water content of the concentrated phosphoric acid becomes large, so that even when an organic poor solvent is added after an inorganic salt aqueous solution has been added, an inorganic salt contained in water in the concentrated phosphoric acid becomes unlikely to be separated out and sometimes, the inorganic salt is not separated out and remains in the concentrated phosphoric acid, so that the purified degree of phosphoric acid is impaired. Thus, it is desired that a phosphoric acid aqueous solution containing a plurality of metal ions which is an object of the treatment is concentrated to a concentration of about 90% by mass or more. When a phosphoric acid aqueous solution which is an object of the treatment has a phosphoric acid concentration of lower than about 90% by mass, the content of water is increased and consequently, a larger amount of an inorganic salt dissolved in the water remains in the filtrate, so that the advantage of the present invention is unlikely to be obtained.

Further, in an embodiment of the present invention, when the amount of metal ions dissolved in a phosphoric acid / organic poor solvent mixture in the coprecipitation process is larger than the amount of metal ions dissolved in the phosphoric acid aqueous solution (that is, concentrated phosphoric acid) before the mixing process, there is substantially no effect of the purification, so that purified phosphoric acid having a high purity cannot be obtained. Therefore, when metal ions dissolved in concentrated phosphoric acid is coprecipitated with a crystallized inorganic salt after the addition of the inorganic salt aqueous solution, it is also important that the inorganic salt is completely crystallized and the remaining of the inorganic salt in the phosphoric acid aqueous solution is prevented.

Further, when the concentration of metal ions which are an object to be removed is low, a ratio of cations constituting the inorganic salt in cations contained in the filtrate after the crystallization and coprecipitation, and the solid-liquid separation becomes large and consequently, the treatment results in nothing but exchanging metal ions desired to be removed with metal ions in the inorganic salt, so that the advantage of the present invention is unlikely to be obtained. Therefore, it is necessary that the concentration of metal ions in the phosphoric acid aqueous solution containing a plurality of metal ions is

higher than a solubility of the inorganic salt in the phosphoric acid / organic poor solvent mixture after the addition of the organic poor solvent. More specifically, the concentration of metal ions in the phosphoric acid aqueous solution which is an object to be treated is preferably around 500 ppm or more based on the weight.

[0011]

As an example of embodiments of the present invention, the method and apparatus for treating a mixed acid aqueous solution waste liquid containing a plurality of metal ions discharged from a metal etching process is described referring to the figures.

FIG. 1 is a schematic view showing an apparatus in a metal etching process which includes a part for performing the etching equipped with a receiving vessel of an etching liquid, a mixed acid aqueous solution tank, a mixed acid aqueous solution waste liquid tank, the purifying apparatus of a mixed acid aqueous solution according to an embodiment of the present invention, and piping connecting these apparatuses. The flow of the process is as follows.

First, a mixed acid aqueous solution new fresh liquid is supplied into the mixed acid aqueous solution tank and next, the mixed acid aqueous solution is pumped up from the mixed acid aqueous solution tank and while showering the solution, a material to be etched is etched.

The mixed acid aqueous solution after the etching is returned to the mixed acid aqueous solution tank as a post-etching liquid through the receiving vessel of an etching liquid.

A mixed acid aqueous solution which has overflowed from the mixed acid aqueous solution tank when the mixed acid aqueous solution new fresh liquid is supplied into the mixed acid aqueous solution tank, is transferred into the mixed acid aqueous solution waste liquid tank as a mixed acid aqueous solution waste liquid.

The mixed acid aqueous solution waste liquid gathered in the mixed acid aqueous solution waste liquid tank is supplied into the purifying apparatus for the mixed acid aqueous solution and metal ions dissolved in the mixed acid aqueous solution during the etching are separated by a crystallization and coprecipitation method and purified. The treated mixed acid aqueous solution is recovered and returned into the mixed acid aqueous solution tank. A part thereof is discharged as a waste liquid out of the system.

[0012]

FIG. 2 is a schematic view showing an evaporating apparatus as a part of the purifying apparatus of a mixed acid aqueous solution. Though the evaporating apparatus may be a general apparatus, a thin film flow down type evaporating apparatus is desired because of a

high viscosity of phosphoric acid. The operation and function of the apparatus is as follows.

First, a mixed acid aqueous solution waste liquid supplied from the mixed acid aqueous solution waste liquid tank in FIG. 1 is supplied through a reboiler into a liquid receiving vessel.

Next, inside the system, the atmosphere is maintained under 2000 to 7000 Pa and the temperature of the liquid is maintained at around 60°C to 90°C. While circulating the mixed acid aqueous solution waste liquid between the liquid receiving vessel and the reboiler using a pump, a steam is supplied to the reboiler to heat the mixed acid aqueous solution waste liquid and nitric acid, acetic acid and water are evaporated to be distilled off.

Nitric acid, acetic acid and water distilled off are condensed in a condenser through which cooling water is supplied, are pooled in a receiver of a distilled liquid and thereafter, are reused as a material for controlling the concentration of the etching liquid.

Concentrated phosphoric acid from which nitric acid, acetic acid and water have been distilled off is transferred to the crystallization and coprecipitation process or the melt crystallization process.

[0013]

FIG. 3 is a schematic view illustrating one example of a metal etching liquid recycle system in which the apparatus for obtaining purified phosphoric acid according to an embodiment of the present invention is incorporated in the online of a metal etching apparatus.

The etching apparatus and the evaporating apparatus are the same apparatuses as those described in FIGS. 1 and 2. Unless otherwise specified, the operating temperature and pressure are normal temperature and pressure.

As described above, the mixed acid aqueous solution waste liquid discharged from the etching apparatus is transferred into the evaporating apparatus and is separated into concentrated phosphoric acid and the distillate (nitric acid, acetic acid and water).

The distillate is transferred into the etching liquid concentration controlling apparatus and is reused.

The concentrated phosphoric acid is transferred into the crystallizing and coprecipitating vessel and is mixed with the inorganic salt aqueous solution which has been beforehand premixed in an inorganic salt dissolving vessel. Examples of the inorganic salt include phosphoric acid salts such as sodium dihydrogen phosphate,

potassium dihydrogen phosphate, ammonium dihydrogen phosphate and magnesium phosphate; sulfates such as sodium sulfate and ammonium sulfate; and acetates such as sodium acetate and ammonium acetate, and phosphates and sulfates are preferred.

When mixed thoroughly, an organic poor solvent is added thereto and by separating out an inorganic salt crystal, simultaneously, the metal in the concentrated phosphoric acid is coprecipitated. The amount of the organic poor solvent is in the volume ratio, 2 to 10 folds, preferably around 3 to 5 folds the volume of phosphoric acid. As the organic poor solvent, those dissolving only around less than 0.1% by mass of inorganic salts such as alcohols and ketones are necessary to be used. Specific examples thereof include isopropyl alcohol (hereinafter, referred to as "IPA"), isobutanol, acetone and methyl isobutyl ketone.

After the completion of the crystallization and coprecipitation, the slurry is transferred into a filtering apparatus to be solid-liquid separated. The filtering apparatus is preferably a filter press- or Nutsche-type filter.

Here, the types and amounts of the inorganic salt and the organic poor solvent may be appropriately determined depending on the metal ion concentration in the concentrated phosphoric acid.

[0014]

The filtrate (mixture of phosphoric acid, organic poor solvent and water) which has passed through the filtering apparatus is transferred into the organic solvent evaporating apparatus and the organic poor solvent and water are distilled off from the filtrate. The organic poor solvent is dehydrated to be purified in an organic solvent dehydrating apparatus and then, is reused in the crystallizing and coprecipitating vessel.

The purified phosphoric acid from which the organic poor solvent has been distilled off is mixed with the distillate from the evaporating apparatus in the etching liquid concentration controlling apparatus and the resultant mixture is supplemented with lacking components so that the mixture has the almost same composition as that of the mixed acid aqueous solution new fresh liquid and is circulatory used as a recycled mixed acid aqueous solution in the etching apparatus.

The method and apparatus of an embodiment of the present invention is suitable for treating a phosphoric acid aqueous solution containing metal ions in high concentration (from 500 ppm based on the weight to an upper limit concentration in which a metal can be dissolved as a metal ion in a phosphoric acid aqueous solution) which is discharged after a primary treatment of a phosphoric acid aqueous solution containing metal ions in a

relatively low concentration (less than 500 ppm based on the weight) by a melt crystallization method or a solvent extraction method.

[0015]

A residue (a coprecipitated metal-containing inorganic salt) in the filtering apparatus is dissolved by supplying water thereto (not illustrated) and is transferred into an inorganic salt crystallizing and purifying vessel. The amount of supplied water is around 1.5 folds the amount of the residue.

In the inorganic salt crystallizing and purifying vessel, a certain amount of water is distilled off from the solution of the residue and the inside of the vessel is cooled to crystallize an inorganic salt. The resultant inorganic salt is retained in the cooled vessel for around 0.5 to 1 hour and then, is transferred into a centrifugal filtering apparatus to separate the inorganic salt into a purified inorganic salt and waste liquid.

The purified inorganic salt is reused in the inorganic salt dissolving vessel.

Since the crystal of the inorganic salt in the crystallizing and coprecipitating vessel is generated according to a localized solubility change at a position to which the organic poor solvent is added and the generated crystal has a coarse crystal form having micropores, so that metal ions are coprecipitated while being adsorbed to this coarse structure. However, in the inorganic salt crystallizing and purifying vessel, by concentrating and cooling the liquid, the whole inside of the vessel is maintained in a homogeneous state, so that the generated crystal becomes rigid and compact and by removing a mother liquor attached to the surface of the crystal using a centrifugal filtering apparatus ($G = 1500$ or more) to purify the crystal, a crystal containing no metal ion at all can be taken out.

[0016]

FIG. 5 is a schematic view illustrating another example of the metal etching liquid recycle system in which the apparatus for obtaining purified phosphoric acid according to an embodiment of the present invention is incorporated in the online of a metal etching apparatus.

A large difference of the system shown in FIG. 5 from that shown in FIG. 3 is that a melt crystallizing apparatus is provided in the upper stream of the crystallizing and coprecipitating vessel and other equipments are substantially the same as those in FIG. 3.

The concentrated phosphoric acid separated in the evaporating apparatus is transferred into the melt crystallizing apparatus and is cooled to around 10°C to separate out a phosphoric acid hemihydrate crystal. Thereafter, the resultant phosphoric acid hemihydrate crystal is solid-liquid separated in the filtering apparatus (not illustrated).

The separated phosphoric acid hemihydrate crystal is heated and dissolved and is transferred into the etching liquid concentration controlling apparatus to supplement lacking components to the dissolved phosphoric acid hemihydrate crystal to prepare a recycled etching liquid. The recycled etching liquid is reused in the metal etching process.

The filtrate in which metal ions are concentrated is transferred into the crystallizing and coprecipitating vessel and is treated in substantially the same manner as that in FIG. 3.

However, when the concentration of metal ions contained in the purified phosphoric acid from which the organic poor solvent is distilled off in the organic solvent evaporating apparatus is in an unsatisfactory level, the purified phosphoric acid may be returned into the melt crystallizing apparatus (a path shown by a broken line in FIG. 5) to be retreated.

FIG. 5 shows an example for providing the melt crystallizing apparatus in the upper stream of the crystallizing coprecipitating vessel. However, since the amount of metal in the phosphoric acid hemihydrate crystal discharged from the melt crystallizing apparatus depends on the metal concentration in the mother liquor, when the metal ion concentration in the concentrated phosphoric acid is extremely high, it is preferred to exchange the positions of the melt crystallizing apparatus and the crystallizing and coprecipitating vessel to each other.

Examples

[0017]

Hereinafter, the present invention is described more specifically referring to Examples which should not be construed as limiting the scope of the present invention.

[0018]

Example 1

Using a recycle system shown in FIG. 3, the treatment of the mixed acid aqueous solution waste liquid from an Al etching process was performed. The unit of the composition is "kg" and "N.D." means at or below a detectable lower limit.

The composition of the mixed acid aqueous solution waste liquid (about 100 kg) discharged from the etching process was as follows. The amount of metal ions other than Al and Mo was extremely small and then, was disregarded.

[Table 1]

Phosphoric acid	Nitric acid	Acetic acid	Water	Al	Mo
65	10	3.5	21.5	0.030	0.045

Further, the composition of the distillate (about 27.8 kg) from the evaporating apparatus was as follows.

[Table 2]

Phosphoric acid	Nitric acid	Acetic acid	Water	Al	Mo
N.D.	10	3.5	14.3	N.D.	N.D.

Further, the composition of concentrated phosphoric acid (about 72.2 kg) which had passed through the evaporating apparatus was as follows.

[Table 3]

Phosphoric acid	Nitric acid	Acetic acid	Water	Al	Mo
65	N.D.	N.D.	7.2	0.030	0.045

[0019]

Next, 7.4 kg of sodium dihydrogen phosphate was dissolved in 10 kg of water and the resultant solution was charged into the crystallizing and coprecipitating vessel and was thoroughly mixed with the concentrated phosphoric acid. After the resultant mixture was thoroughly stirred, while stirring the mixture, 260 kg of IPA anhydride was added to the mixture. At this step, the composition of the treated liquid (about 349.6 kg) was as follows.

Here, Na is derived from an inorganic salt and is contained in an inorganic substance. For a convenience of explaining with respect to metal ions, the composition thereof was also cited. It is the same with respect to the below-described filtrate, residue and purified phosphoric acid.

[Table 4]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
65	17.2	7.4	260	0.030	0.045	1.43

Further, the composition of the filtrate (about 338.7 kg) which had passed through the filtering apparatus was as follows.

[Table 5]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
64	16.7	0.04	258	0.003	0.016	0.008

Further, the residue (about 10.9 kg) in the filtering apparatus was as follows.

[Table 6]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
1	0.5	7.36	2	0.027	0.029	1.422

When the amounts of Al, Mo in the above filtrate and in the above residue are compared to each other, Al, Mo are shifted predominantly to the residue (coprecipitated), so that it is apparent that by this treatment, Al, Mo in the concentrated phosphoric acid are separated out. However, by adding the inorganic salt into the concentrated phosphoric acid, Na ions are added thereto. Thus, Na ions are necessary to be removed as much as possible and further, for enhancing the purity of the phosphoric acid, inorganic substances dissolved in the concentrated phosphoric acid are also necessary to be removed as much as possible.

[0020]

Next, the filtrate was transferred into the organic solvent evaporating apparatus to evaporate and separate IPA and water from the filtrate, and IPA was recovered in a distilling apparatus for recovering IPA (not illustrated) and was reused. Further, for distilling off IPA completely from the phosphoric acid, water was added to the phosphoric acid from which IPA had been distilled off and IPA was reevaporated together with water to perform deliquoring by azeotropy. From the bottom of the organic solvent evaporating apparatus, purified phosphoric acid was obtained.

The composition of the obtained purified phosphoric acid (about 71.1 kg) was as follows.

[Table 7]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
64	7.1	0.04	N.D.	0.003	0.016	0.008

The above composition is of the purified phosphoric acid which has been subjected to one time of the crystallizing and coprecipitating treatment. However, when the composition is not satisfactory, it is satisfactory to perform these treatments one more time to remove metal ions. Such a treatment is exemplified as follows.

Since the concentration of metal ions in the mother liquor was lower than that in the first treatment, the second treatment was performed by adding the inorganic salt (sodium dihydrogen phosphate) in an amount of 1/5 of that in the first treatment.

The composition of the obtained purified phosphoric acid (about 70.5 kg) was as follows and purified phosphoric acid having a higher purity could be obtained.

[Table 8]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
63.5	7.0	0.02	N.D.	0.00004	0.00061	0.004

[0021]

The above residue (about 10.9 kg) was transferred into the inorganic salt crystallizing and purifying vessel and was treated and the composition of the obtained purified inorganic salt (about 7.5 kg) was as follows. The purified inorganic salt was reused in the inorganic salt dissolving vessel and there was no problem.

[Table 9]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
N.D.	0.5	7.0	N.D.	N.D.	N.D.	1.34

As described above, according to the system of an example the present invention, about 98% by mass of phosphoric acid in the mixed acid aqueous solution waste liquid can be reused and a charging amount of the mixed acid aqueous solution new fresh liquid can be largely reduced.

[0022]

Example 2

The treatment of the mixed acid aqueous solution waste liquid from an Al etching process was performed in substantially the same manner as in Example 1.

The compositions of the mixed acid aqueous solution waste liquid (about 100 kg) discharged from the etching process, the distillate (about 27.8 kg) from the evaporating apparatus and concentrated phosphoric acid (about 72.2 kg) which had passed through the evaporating apparatus were the same as those in Example 1.

Next, the treatments were performed in substantially the same manner as in Example 1, except that the inorganic salt was changed to 4.43 kg of sodium sulfate and was used by dissolving the salt in 18 kg of water. At this step, the composition of the treated liquid (about 354.6 kg) was as follows.

The relationship between the Na amount and the inorganic salt amount is the same as that in Example 1.

[Table 10]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
65	25.2	4.43	260	0.030	0.045	1.43

Further, the composition of the filtrate (about 346.5 kg) which had passed through the

filtering apparatus was as follows.

[Table 11]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
64	24.5	0.02	258	0.002	0.010	0.006

Further, the residue (about 8.1 kg) in the filtering apparatus was as follows.

[Table 12]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
1	0.7	4.41	2	0.028	0.035	1.424

When the amounts of Al, Mo in the above filtrate and in the above residue are compared to each other, Al, Mo are shifted predominantly to the residue (coprecipitated), so that it is apparent that by this treatment, Al, Mo in the concentrated phosphoric acid are separated out. However, by adding the inorganic salt into the concentrated phosphoric acid, Na ions and SO_4^{2-} ions are added thereto. Thus, these ions are necessary to be removed as much as possible and further, for enhancing the purity of the phosphoric acid, inorganic substances dissolved in the concentrated phosphoric acid are also necessary to be removed as much as possible.

Next, the filtrate was supplied into the organic solvent evaporating apparatus and the treatment was performed in substantially the same manner as in Example 1. As a result, the composition of the obtained purified phosphoric acid (about 71.1 kg) was as follows. As SO_4^{2-} ions, SO_4^{2-} ions constituting sodium sulfate salt together with Na (0.006 kg) which could not be removed and remained slightly, remained.

[Table 13]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
64	7.1	0.02	N.D.	0.002	0.010	0.006

[0023]

Example 3

Using a recycle system shown in FIG. 3, the treatment of the mixed acid aqueous solution waste liquid from an Al etching process was performed in substantially the same manner as in Example 1. FIG. 4 shows a material balance per each fundamental block.

In this Example, for maintaining the concentration of metal ions (total of Al, Mo and Na) in the mixed acid aqueous solution tank to 500 ppm or less based on the weight, when it is assumed that the treating amount of the mixed acid aqueous solution waste liquid is 100 kg/h; the amount of the recycled mixed acid aqueous solution is 90 kg/h; the concentration of metal ions in the recycled mixed acid aqueous solution is suppressed to 30

ppm or less; and the mixed acid aqueous solution new fresh liquid (for supplementation) is supplemented in an amount of 10 kg/h, the upper limit of the amount of etched metals is, as shown by the following equation 0.0473 kg/h.

$$100 \text{ kg/h} \times 0.0005 - 100 \text{ kg/h} \times 0.9 \times 0.00003 = 0.0473 \text{ kg/h}$$

[0024]

Example 4

Using a recycle system shown in FIG. 5, the treatment of the mixed acid aqueous solution waste liquid from an Al etching process was performed. The compositions of the mixed acid aqueous solution waste liquid (about 100 kg) discharged from the etching process, the distillate (about 27.8 kg) from the evaporating apparatus and concentrated phosphoric acid (about 72.2 kg) which had passed through the evaporating apparatus were the same as those in Example 1.

Next, the concentrated phosphoric acid was transferred into the melt crystallizing apparatus and was cooled to about 10°C to crystallize a phosphoric acid hemihydrate crystal. Next, the resultant phosphoric acid hemihydrate crystal was solid-liquid separated in the filtering apparatus. Thereafter, the separated phosphoric acid hemihydrate crystal was heated and dissolved and was transferred into the etching liquid concentration controlling apparatus to supplement lacking components to the dissolved phosphoric acid hemihydrate crystal to prepare a recycled etching liquid. The recycled etching liquid was reused in the metal etching process. The composition of the obtained phosphoric acid hemihydrate crystal is as follows.

[Table 14]

Phosphoric acid	Water	Al	Mo
52	4.8	0.001	0.0015

Further, the composition of the filtrate is as follows.

[Table 15]

Phosphoric acid	Water	Al	Mo
13	2.4	0.029	0.0435

The above filtrate was transferred into the crystallizing and coprecipitating vessel and was treated in substantially the same manner as in Example 1. As a result, the composition of the obtained purified phosphoric acid (13.8 kg) was as follows.

[Table 16]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
12.4	1.4	0.01	N.D.	0.0008	0.0035	0.002

The above purified phosphoric acid was returned to the melt crystallizing process and was treated again in substantially the same manner as in the above treatment. As a result, purified phosphoric acid having the following composition was obtained.

[Table 17]

Phosphoric acid	Water	Inorganics	IPA	Al	Mo	(Na)
9.9	0.9	0.0003	N.D.	0.00003	0.0001	0.00007

It is apparent that by repeating the melt crystallizing as described above, purified phosphoric acid having a higher concentration can be obtained.

[0025]

Example 5

Using a recycle system shown in FIG. 5, the treatment of the mixed acid aqueous solution waste liquid from an Al etching process was performed in substantially the same manner as in Example 1. FIG. 6 shows a material balance per each fundamental block.

In this Example, for maintaining the concentration of metal ions (total of Al, Mo and Na) in the mixed acid aqueous solution tank to 500 ppm or less based on the weight, when it is assumed that the treating amount of the mixed acid aqueous solution waste liquid is 100 kg/h; the amount of the recycled mixed acid aqueous solution is 98 kg/h; the concentration of metal ions in the recycled mixed acid aqueous solution is suppressed to 30 ppm or less; and the mixed acid aqueous solution new fresh liquid (for supplementation) is supplemented in an amount of 2 kg/h, the upper limit of the amount of etched metals is, as shown by the following equation 0.04706 kg/h.

$$100 \text{ kg/h} \times 0.0005 - 100 \text{ kg/h} \times 0.98 \times 0.00003 = 0.04706 \text{ kg/h}$$

What is claimed is:

1. A method for obtaining purified phosphoric acid comprising:

[1] crystallizing and coprecipitating that separate out an inorganic salt crystal from a phosphoric acid aqueous solution containing a plurality of metal ions and coprecipitate metal ions comprising:

(a) mixing a phosphoric acid aqueous solution containing a plurality of metal ions with an inorganic salt aqueous solution selected from a group consisting of sodium dihydrogen phosphate, potassium dihydrogen phosphate, magnesium phosphate, sodium sulfate and sodium acetate;

(b) separating out an inorganic salt crystal and coprecipitating simultaneously the metal ions by further mixing an organic poor solvent which is soluble in phosphoric acid and does not dissolve an inorganic salt with the above resultant mixture; and

(c) solid-liquid separating by filtering the inorganic salt crystal containing the metal ions; and

[2] evaporating that obtains purified phosphoric acid by evaporating an organic poor solvent and water in a filtrate obtained by the filtration;

wherein the amount of metal ions dissolved in the phosphoric acid / organic poor solvent mixture in the separating out is less than the amount of metal ions in the phosphoric acid solution used in the mixing.

2. The method for obtaining purified phosphoric acid according to claim 1, wherein the crystallizing and coprecipitating and the evaporating are repeated further in plural times with respect to the purified phosphoric acid obtained by the method according to claim 1 to obtain purified phosphoric acid having a higher concentration.

3. The method for obtaining purified phosphoric acid according to claim 1 or 2, wherein the phosphoric acid aqueous solution containing a plurality of metal ions contains metal ions in a concentration of from 500 ppm based on the weight to an upper limit concentration in which a metal can be dissolved as a metal ion in the phosphoric acid aqueous solution.

4. The method for obtaining purified phosphoric acid according to any one of claims 1 to 3, wherein the inorganic salt crystal containing metal ions obtained in the crystallizing and coprecipitating is dissolved in water; the inorganic salt crystal is separated out by cooling to separate a coprecipitated metal from the inorganic salt; the inorganic salt is filtered to be

recovered; from the recovered inorganic salt, an aqueous solution of the inorganic salt is prepared; and the prepared inorganic salt aqueous solution is reused in the mixing according to claim 1.

5. An apparatus for preparing purified phosphoric acid when used for performing the method according to any one of claims 1 to 3 comprising at least:

- an inorganic salt dissolving vessel for preparing an inorganic salt aqueous solution;
- a crystallizing and coprecipitating vessel in communication with the inorganic salt dissolving vessel comprising a stirrer for mixing the inorganic salt aqueous solution with a phosphoric acid aqueous solution to obtain an inorganic salt crystal, wherein the phosphoric acid aqueous solution contains a plurality of metal ions and an organic solvent;

- a filtering apparatus in communication with the crystallizing and coprecipitating vessel comprising a mean to separate the crystal from the solutions to obtain a filtrate; and

- an evaporating apparatus in communication with the filtering apparatus comprising a heating unit to heat the filtrate.

6. The apparatus according to claim 5, wherein the crystallizing and coprecipitating vessel further provides for coprecipitating the metal ions simultaneously.

7. The apparatus according to claim 5 or 6, wherein the evaporating apparatus provides for the evaporation of the solvent and water from the filtrate.

8. The apparatus according to any one of claims 5-7, further comprising:

- an inorganic salt crystallizing and purifying vessel in communication with the filtering apparatus comprising

- a stirrer for dissolving the crystal present in the filtrate in warm water; and

- a mean for cooling, the dissolved mixture to obtain a further inorganic salt crystal;

and

- a further filtering apparatus in communication with the inorganic salt crystallizing and purifying vessel comprising a mean for separating the further crystal.

9. A method for reusing an etching liquid comprising:

recovering an used mixed acid aqueous solution waste liquid containing a plurality of metal ions generated in a metal etching using a mixed acid aqueous solution composed of phosphoric acid, nitric acid, acetic acid and water;

evaporating that fractionally-distills the mixed acid aqueous solution waste liquid by evaporating nitric acid, acetic acid and most of water from the mixed acid aqueous solution waste liquid into a distillate containing nitric acid, acetic acid and water and concentrated phosphoric acid containing phosphoric acid and a plurality of metal ions;

purificating that obtains purified phosphoric acid by coprecipitating and separating the metal ions in the concentrated phosphoric acid using the apparatus according to any one of claims 5-8; and

concentration controlling that controls a liquid concentration by adding the distillate to the obtained purified phosphoric acid to prepare a recycled mixed acid aqueous solution and uses the recycled mixed acid aqueous solution again in the metal etching.

10. The method for reusing an etching liquid according to claim 9, further comprising separating out that comprises:

separating out a phosphoric acid hemihydrate crystal from the concentrated phosphoric acid obtained in the evaporating using a melt crystallizing apparatus;

solid-liquid separating the phosphoric acid hemihydrate crystal using a filtering apparatus;

transferring the obtained phosphoric acid hemihydrate crystal into the concentration controlling; and

transferring the filtrate obtained from the solid-liquid separation in which metal ions are concentrated into the crystallizing and coprecipitating vessel according to any one of claims 5-8.