

DESCRIPTION

Title of the Invention: METHOD FOR PRODUCING PURIFIED
ISOPROPYL ALCOHOL AQUEOUS SOLUTION

TECHNICAL FIELD

[0001]

The present invention relates to a method for producing a purified isopropyl alcohol aqueous solution and a method for producing purified isopropyl alcohol.

BACKGROUND ART

[0002]

Isopropyl alcohol (hereinafter, also abbreviated as "IPA") has a property of dissolving both water and an organic solvent, and is widely used as a solvent for paints and inks, various synthetic raw materials, and the like. Further, IPA having high purity is used in a large amount also in a rinsing unit of semiconductor substrates provided in a semiconductor manufacturing device, and an increase in the usage amount is expected in the future.

[0003]

The production cost of IPA having high purity is high, and the rinsing unit for semiconductor substrates in which IPA is used in a large amount may be a factor of cost increase. In addition, the IPA waste liquid after use is normally subjected to a combustion treatment, but carbon dioxide, which is

considered to be a cause of global warming, is released in this case, so that it has been desired to reduce the waste amount thereof also from the viewpoint of environmental protection. Therefore, there is an increasing demand for recovering, purifying, and reusing the IPA waste liquid discharged from such industrial facilities (for example, see Patent Document 1).

[0004]

Incidentally, the rinsing unit for semiconductor substrates is generally provided adjacent to a later stage of a cleaning unit of semiconductor substrates. Since ultrapure water or a high-water-content liquid is normally used as the cleaning liquid used in the cleaning unit, moisture adhering to surfaces of the semiconductor substrate in the cleaning unit is washed down by the rinsing unit. Therefore, the IPA waste liquid recovered from the rinsing unit tends to become a low-water-content composition containing a small amount of water. In addition, IPA is also often used in a developing unit and a pre-wetting unit, and water is also often used in various parts of the semiconductor manufacturing devices. Therefore, a low-water-content IPA waste liquid is normally discharged from the semiconductor manufacturing device including the rinsing unit and, for example, in Patent Document 2, the content of water in the low-water-content IPA waste liquid is assumed to be about 5% by mass.

[0005]

On the other hand, in semiconductor manufacturing

devices, toluene may be used in the cleaning unit or the rinsing unit, and toluene is also widely used as a solid solvent, for example, a solvent component of a photoresist material used in the developing unit or a solvent component of an adhesive used in the various units. Further, compounds containing a toluene sulfonyl group are often used in substrate treatment agents, and toluene may be generated when the compounds decompose. For this reason, a trace amount of toluene may be mixed into the recovered IPA waste liquid.

[0006]

Accordingly, a low-water-content IPA waste liquid containing toluene (hereinafter, also simply referred to as "low-water-content IPA waste liquid") may be recovered as an impurity from industrial facilities such as semiconductor manufacturing devices including a rinsing unit, and purification treatment of the low-water-content IPA waste liquid is performed. In general, a typical purification method of organic solvents includes distillation and, for example, Patent Document 3 proposes purifying a low-water-content IPA waste liquid, which may contain toluene or the like as an impurity with a water content of 5% to 15%, by a purification process applying distillation.

Citation List

Patent Documents

[0007]

Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2017-144410

Patent Document 2: Japanese Unexamined Patent Application,
Publication No. 2014-55120

Patent Document 3: Chinese Patent Application, Publication No.
112999679

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0008]

However, in a case where toluene is contained in the low-water-content IPA waste liquid, it is difficult to remove toluene to a high degree by a distillation method in the related art. For example, in Patent Document 3, in the purification process, the IPA waste liquid is supplied to a rectifying column to perform rectification, and a fraction containing IPA is obtained from the column top. Then, the fraction containing IPA is cooled to liquify, then supplied to a phase separation device to remove the aqueous phase, then further supplied to a collection tank to be heated, and fractionated into a low-boiling fraction to be supplied to a low-boiling tank and a purified IPA fraction to be recovered in a product tank. However, in a case where the purification process is applied to the purification of the low-water-content IPA waste liquid containing toluene, satisfactory results were not obtained. This is because, although the boiling point (110.6°C) of toluene is higher than the boiling point (82.4°C) of IPA and the boiling point of water, at the time of distillation, toluene and IPA are azeotropic, and IPA

and water are azeotropic, so that a certain amount of toluene is carried along with the fraction containing IPA from the column top of the rectifying column. Since it is difficult to remove toluene carried along with the fraction containing IPA to a high degree by phase separation of the aqueous phase and fractionation operation thereafter, IPA having high purity cannot be obtained.

[0009]

Accordingly, a method for producing a purified isopropyl alcohol aqueous solution and purified isopropyl alcohol having high purity by removing toluene to a high degree from a low-water-content isopropyl alcohol waste liquid containing toluene as an impurity has not been known, and development of this method has been a big problem.

Means for Solving the Problems

[0010]

In view of the above problems, the present inventors have continued intensive studies. As a result, the present inventors have found that a bottom product in which toluene is removed to a high degree can be obtained from a column bottom of a distillation column by adjusting the content of water to be in a specific range with respect to a low-water-content isopropyl alcohol waste liquid containing toluene as an impurity, and have completed the present invention.

[0011]

Specifically, an aspect of the present invention is a method for producing a purified isopropyl alcohol aqueous

solution from a low-water-content isopropyl alcohol waste liquid containing toluene as an impurity, the method including: a low-boiling distillation step of supplying the low-water-content isopropyl alcohol waste liquid to a raw material supply stage of a distillation column, extracting a distillate containing toluene from a column top of the distillation column, and extracting a bottom product containing isopropyl alcohol and water from a column bottom of the distillation column, in which a content of water in a liquid phase in the raw material supply stage of the distillation column is adjusted to 70% by mass or more and 95% by mass or less.

[0012]

In such a method for producing a purified isopropyl alcohol aqueous solution, it is preferable that the low-water-content isopropyl alcohol waste liquid is a waste liquid recovered from a semiconductor manufacturing device including a rinsing unit for semiconductor substrates.

[0013]

In addition, it is preferable that the content of water in the liquid phase in the raw material supply stage of the distillation column is adjusted to 80% by mass or more and 93% by mass or less.

[0014]

In addition, it is preferable that a content of toluene in the low-water-content isopropyl alcohol waste liquid is 1 ppm or more and 2,000 ppm or less in terms of mass ratio

relative to isopropyl alcohol.

[0015]

Further, another aspect of the present invention is a method for producing purified isopropyl alcohol from a purified isopropyl alcohol aqueous solution obtained by such a method for producing a purified isopropyl alcohol aqueous solution, the method including: a dehydration step of dehydrating the purified isopropyl alcohol aqueous solution.

[0016]

In such a method for producing purified isopropyl alcohol, it is preferable that the method further includes: an azeotropic mixture generation step of distilling the purified isopropyl alcohol aqueous solution and extracting an azeotropic mixture of isopropyl alcohol and water as a distillate; and a dehydration step of adding an azeotropic agent to the azeotropic mixture of isopropyl alcohol and water to perform distillation, and extracting a bottom product containing isopropyl alcohol to perform dehydration.

[0017]

In addition, it is preferable that the purified isopropyl alcohol is a semiconductor chemical liquid. In particular, it is preferable that the semiconductor chemical liquid is a rinsing liquid for semiconductor substrates.

[0018]

In addition, it is preferable that the method further includes: a second low-boiling distillation step of subjecting the azeotropic mixture which was dehydrated to low-boiling

distillation to extract a bottom product containing isopropyl alcohol; and a high-boiling distillation step of subjecting the bottom product containing isopropyl alcohol to high-boiling distillation to extract a distillate containing isopropyl alcohol.

Effects of the Invention

[0019]

According to the present invention, toluene can be removed to a high degree from the low-water-content IPA waste liquid containing toluene as an impurity. Accordingly, the low-water-content IPA waste liquid can be easily regenerated into IPA having high purity, and IPA having high purity can be favorably reused as a semiconductor chemical liquid, in particular, a rinsing liquid of semiconductor substrates, and the industrial value is extremely large.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Fig. 1 is a schematic view illustrating a typical embodiment of a low-boiling distillation step; and Fig. 2 is a graph illustrating the influence of moisture concentration on the relative volatility α of toluene with respect to IPA.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0021]

Hereinafter, embodiments of the present invention will be

described with reference to the drawings.

[0022]

[Method for Producing Purified IPA Aqueous Solution]

(Low-water-content IPA Waste Liquid)

In the present embodiment, a target liquid for distillation is a low-water-content IPA waste liquid containing toluene as an impurity. The low-water-content IPA waste liquid is often discharged from the production of paint and ink and various industrial facilities using the same, and a waste liquid to be recovered can be applied without limitation, but a waste liquid recovered from a semiconductor manufacturing device including a rinsing unit of semiconductor substrates is most suitable for purification. In particular, the waste liquid recovered from the rinsing unit easily becomes a low-water-content composition, and can be suitably applied. In addition, a developing solution, a pre-wet liquid, an etching solution, a cleaning liquid, a stripping liquid, and a drying liquid discharged from the semiconductor manufacturing device may be contained in the low-water-content IPA waste liquid.

[0023]

The content of IPA in the low-water-content IPA waste liquid is preferably more than 50% by mass, more preferably 60% by mass or more, and particularly preferably 70% by mass or more. The content of IPA in the low-water-content IPA waste liquid is preferably 95% by mass or less, and more preferably 85% by mass or less.

[0024]

In the present disclosure and claims, "low-water-content" indicates that the content of water is less than 50% by mass. The content of water in the low-water-content IPA waste liquid is preferably 40% by mass or less, and more preferably 30% by mass or less. The content of water in the low-water-content IPA waste liquid is preferably 5% by mass or more, and more preferably 15% by mass or more. In a case where the content of water in the low-water-content IPA waste liquid is large, equipment for recovering the low-water-content IPA waste liquid becomes enormous, and the cost for transporting the low-water-content IPA waste liquid increases.

[0025]

Here, the content of water in the low-water-content IPA waste liquid is a value measured by the Karl Fischer method. In addition, the content of IPA in the low-water-content IPA waste liquid is a value measured by gas chromatography.

[0026]

The content of toluene in the low-water-content IPA waste liquid is preferably 1 ppm or more and 2,000 ppm or less, and more preferably 50 ppm or more and 1,000 ppm or less in terms of mass ratio relative to isopropyl alcohol. When the content of toluene in the low-water-content IPA waste liquid is equal to or larger than a lower limit value, an effect of removing toluene is remarkably exhibited. On the other hand, when the content of toluene in the low-water-content IPA waste liquid is equal to or less than an upper limit value, toluene and IPA

are hardly azeotropic, and the content of toluene in a purified IPA aqueous solution is easily reduced.

[0027]

The low-water-content IPA waste liquid may further contain a low-boiling impurity having a boiling point lower than that of IPA as an impurity other than toluene. Examples of the low-boiling impurity include olefins such as butenes, pentenes, and hexenes; alkanes such as butane, pentane, and hexane; aldehydes such as formaldehyde, acetaldehyde, propylene aldehyde, and butyl aldehyde; ketones such as acetone and butanone; alcohols such as methanol, ethanol, and 2-methyl-2-propanol; and chloroalkanes such as dichloromethane, chloroform, carbon tetrachloride, and vinyl chloride. The total content of the low-boiling impurities in the low-water-content IPA waste liquid is preferably 0.1 ppm or more and 10,000 ppm or less, and more preferably 1 ppm or more and 100 ppm or less in terms of mass ratio relative to IPA. The low-boiling impurities are distilled off to a high degree together with toluene from the column top of a distillation column as will be described later.

[0028]

Further, the low-water-content IPA waste liquid may further contain a high-boiling impurity having a boiling point higher than that of IPA as the impurity other than toluene. Specifically, in a case where the low-water-content IPA waste liquid is a waste liquid of a semiconductor chemical liquid, in particular, a cleaning liquid or a drying liquid, examples

of the high-boiling impurity include metals such as iron, chromium, nickel, copper, zinc, sodium, potassium, calcium, and magnesium; carboxylic acids such as formic acid, acetic acid, and propionic acid; salts having nitrate ion, nitrite ion, sulfate ion, chloride ion, fluoride ion, and the like as an anion; aldehydes and ketones such as crotonaldehyde and 2-pentanone; alcohols such as 1-propanol and 1-butanol; ethers such as 1-methoxy-2-propanol, 1-(2-methoxypropoxy) propane-2-ol, and 1-(2-methoxy-2-methylethoxy)-2-propanol; aromatic compounds such as toluene and xylene (ortho-, meta-, and para-); alkanes such as octane, decane, and hexadecane; carboxylic acid esters such as isopropyl acetate, isopropyl propionate, and butyl formate; phthalic acid esters such as dioctyl phthalate and dibutyl phthalate; and adipic acid esters such as dioctyl adipate. As will be described later, the high-boiling impurity can be removed to a high degree by subjecting the bottom product extracted from the column bottom of the distillation column to a purification step to be described later.

[0029]

(Adjustment of Content of Water in Liquid Phase in Raw Material Supply Stage of Distillation Column)

In the present embodiment, for example, when the low-water-content IPA waste liquid recovered from the semiconductor manufacturing device is distilled, the content of water in the liquid phase in the raw material supply stage of the distillation column is adjusted to 70% by mass or more

and 95% by mass or less, and more preferably 80% by mass or more and 93% by mass or less. Accordingly, toluene can also be favorably distilled off together with the low-boiling impurity from the column top of the distillation column. In other words, the bottom product in which toluene is reduced to a high degree can be extracted from the column bottom of the distillation column.

[0030]

Since toluene has a boiling point higher than that of IPA, it is considered that toluene is not distilled off from the column top, but rather discharged from the column bottom when only the boiling point difference is taken into consideration at the time of distillation. However, toluene exhibits a property of being azeotropic with IPA and water, and in such an azeotropic system, toluene is concentrated in the gas phase. In the low-water-content IPA waste liquid, toluene is azeotropic with water, and the concentration in the gas phase becomes dominant. As a result, as illustrated in Fig. 2, as the moisture concentration, that is, the content of water in the liquid phase, increases, the concentration efficiency of toluene to the gas phase is significantly increased.

[0031]

However, in the case of a low-water-content IPA waste liquid, since the content of water is low, it is considered that the concentration efficiency of toluene to the gas phase portion due to the azeotropism with water is insufficient, and

the amount of toluene distilled off from the column top of the distillation column is also low. In the present embodiment, by increasing the content of water in the liquid phase in the raw material supply stage of the distillation column, the azeotropism with water is activated at the time of distillation, and the amount of toluene distilled off from the column top of the distillation column is increased. As a result, the content of toluene in the bottom product is reduced.

[0032]

Examples of the organic solvent include xylene (ortho-, meta-, and para-) and isopropyl acetate, the organic solvents having a boiling point higher than that of IPA and having a property of being azeotropic with IPA, similar to toluene, and being capable to be contained in the waste liquid recovered from the semiconductor manufacturing device. By applying the method for producing a purified IPA aqueous solution of the present embodiment, the same effect is exhibited on such an organic solvent.

[0033]

As a method for adjusting the content of water in the liquid phase in the raw material supply stage of the distillation column, a method is generally used that mixes water after measuring the content of water in a waste liquid receiving tank in which the recovered low-water-content IPA waste liquid is accommodated. In this case, for example, at least two waste liquid receiving tanks are installed, one of

which is used to supply a liquid having adjusted water content to the distillation column, and the other is used to adjust the content of water. In this case, it is efficient to switch the functions of the two tanks when the capacity of the tank used for supply to the distillation column becomes close to empty.

[0034]

The measurement of the content of water with respect to the low-water-content IPA waste liquid and the mixing of water may be performed in a pipe for supplying the low-water-content IPA waste liquid to the distillation column, or may be performed in a transport container (for example, lorry, container, or drum can) when the low-water-content IPA waste liquid is transported to a remote waste liquid receiving tank.

[0035]

The content of water in the liquid phase in the raw material supply stage of the distillation column may be adjusted in the distillation column. That is, while the low-water-content IPA waste liquid is supplied to the raw material supply stage of the distillation column as it is or in a water-added state in which the content of water is less than 70% by mass, water may be supplied to the distillation column from the outside. In this case, water may be supplied to the raw material supply stage of the distillation column, or water may be supplied to a stage between the raw material supply stage of the distillation column and the column top.

[0036]

In the case where water is supplied to the stage between the raw material supply stage of the distillation column and the column top, the content of water in the liquid phase in the raw material supply stage can be determined using process simulation software such as Aspen Plus (produced by Aspen Technology Inc) or PROII (produced by AVEVA). As will be described later, in a case where a distillate from the column top of the distillation column is condensed by a condenser and a part of the condensed distillate is refluxed to the distillation column, the content of water in the liquid phase in the raw material supply stage of the distillation column may be calculated also taking consideration of the amount of water contained in the refluxed distillate. In addition, in a case where the distillate extracted from the column top of the distillation column is supplied to a second distillation column, water is added from the outside, distillation is performed again, and the bottom product is supplied to the distillation column, the content of water in the liquid phase in the raw material supply stage of the distillation column may be calculated also taking consideration of the amount of water contained in the bottom product.

[0037]

The content of water in the liquid phase in the raw material supply stage of the distillation column is not limited as long as the content of water is in a range of 70% by mass or more and 95% by mass or less, but fluctuation per hour is preferably 3% by mass or less, and more preferably 1%

by mass or less, with respect to the total content (100% by mass) of the liquid phase. When the fluctuation per hour is reduced, the boiling point of toluene does not greatly change, and flooding is less likely to occur.

[0038]

(Low-boiling Distillation Step)

The method for producing a purified IPA aqueous solution according to the present embodiment includes a low-boiling distillation step of distilling a low-water-content IPA waste liquid, extracting a distillate containing toluene from the column top of a distillation column, and extracting a bottom product containing IPA and water from the column bottom of the distillation column.

[0039]

Fig. 1 illustrates a typical embodiment of the low-boiling distillation step. That is, in Fig. 1, two waste liquid receiving tanks 1 are installed, one of which is used to supply, to a low-boiling distillation column 2, the low-water-content IPA waste liquid having adjusted water content, and the other is used to adjust the content of water of the low-water-content IPA waste liquid. The functions of both are switched when the low-water-content IPA waste liquid in which the content of water is adjusted becomes empty. The low-water-content IPA waste liquid is supplied to the waste liquid receiving tank 1 through a waste liquid supply pipe 3. In the waste liquid receiving tank 1, water is supplied through a water supply pipe 8 such that the content of water in the

liquid phase in the raw material supply stage of the low-boiling distillation column 2 is 70% by mass or more and 95% by mass or less.

[0040]

Thus, the low-water-content IPA waste liquid having adjusted water content is supplied to the raw material supply stage of the low-boiling distillation column 2 through a distillation target liquid supply pipe 4, and distilled. A condenser 5 is installed at the column top of the low-boiling distillation column 2, a part of a condensate liquid condensed by the condenser 5 is refluxed, and the remainder is discharged as a low-boiling substance distillate through a distillate discharge pipe 6. Toluene contained in the low-water-content IPA waste liquid is carried along with the low-boiling substance distillate, and discharged. As a result, the bottom product from which toluene is removed to a high degree is discharged from the column bottom of the low-boiling distillation column 2 through a bottom product discharge pipe 7.

[0041]

The low-boiling distillation column 2 may be either a tray column or a packed column, but is preferably a tray column. The number of theoretical stages of the low-boiling distillation column 2 is not particularly limited, and is preferably 10 stages to 200 stages, and more preferably 20 stages to 50 stages. Examples of the trays in the tray column include a crossflow tray and a shower tray. Examples of the

packing in the packed column include Raschig rings and Lessing rings. Examples of materials of the tray column, packed column, and packing include iron, stainless steel, hastelloy, borosilicate glass, quartz glass, and fluororesins (for example, polytetrafluoroethylene).

[0042]

In the low-boiling distillation column 2, the number of stages up to the column bottom of the raw material supply stage is preferably 5 or more, more preferably 10 or more, and more preferably 20 or more in terms of the number theoretical stages. When the number of stages of the raw material supply stage up to the column bottom is large, toluene is easily removed. In this case, the raw material supply stage may be installed in a space up to the column top, but the raw material supply stage is preferably installed at the column top because the waste amount of IPA is reduced. In calculation of the raw material supply stage, the column bottom and the column top are not included in the theoretical stages. It is preferable to confirm the number of theoretical stages of the low-boiling distillation column 2 by actually operating the low-boiling distillation column 2 and analyzing the composition of the distillate.

[0043]

The amount of substance in the gas phase at the column top of the low-boiling distillation column 2 is preferably 0.1 to 10 with respect to the amount of substance in the entire liquid phase supplied to the low-boiling distillation column

2.

[0044]

Further, the pressure (gauge pressure) at the column top of the low-boiling distillation column 2 is not particularly limited and is, for example, 0.0 MPaG or more and 0.1 MPaG or less. In this case, temperatures of the column top and the column bottom of the low-boiling distillation column 2 are appropriately set according to the pressure.

[0045]

The low-boiling substance distillate distilled off from the column top is condensed by the condenser 5, and a part of the condensed low-boiling substance distillate is refluxed. In this case, the reflux ratio is preferably 10 or more and 10,000 or less, more preferably 100 or more and 2,000 or less, and even more preferably 300 or more and 1,500 or less. By increasing the reflux ratio, the distillate is reduced, and thus it is possible to separate toluene while reducing the IPA to be distilled off.

[0046]

As described above, the low-boiling substance distillate extracted from the column top may be discharged to the outside of the system, but the low-boiling substance distillate may be supplied to the second distillation column, water may be added from the outside to perform distillation again, and the bottom product may be supplied to an upstream portion of the low-boiling distillation column 2 to further increase the removal characteristics of toluene and low-boiling impurities. The

low-boiling substance distillate discharged to the outside of the system may be reused as a fuel, for example.

[0047]

(Purification Degree of Purified IPA Aqueous Solution)

According to the method for producing a purified IPA aqueous solution of the present embodiment, in the low-boiling distillation step, the content of toluene contained as an impurity can be reduced to preferably 10 ppb or less, and more preferably 0.001 ppb or more and 1 ppb or less in terms of mass ratio relative to IPA. In addition, in a case where the low-boiling impurities can also be reduced to a high degree, for example, aldehydes and ketones such as acetaldehyde and propionaldehyde are contained in the low-water-content IPA waste liquid, it is also possible to reduce their respective contents to preferably 10 ppb or less, and more preferably 0.001 ppb or more and 1 ppb or less in terms of mass ratio relative to IPA.

[0048]

[Method for Producing Purified IPA]

In the low-boiling distillation step, purified IPA can be produced by dehydrating the purified IPA aqueous solution serving as the bottom product extracted from the column bottom of the low-boiling distillation column 2. In order to obtain purified IPA having higher purity, the following additional purification step is preferably performed. That is, the additional purification step includes an azeotropic mixture generation step of distilling the purified IPA aqueous

solution and extracting an azeotropic mixture of IPA and water as a distillate, and a dehydration step of dehydrating the azeotropic mixture of IPA and water.

[0049]

It is preferable that the additional purification step further includes a high-boiling distillation step of subjecting the dehydrated azeotropic mixture to high-boiling distillation to extract a distillate containing isopropyl alcohol. In addition, in order to remove the low-boiling impurities to a higher degree, a second low-boiling distillation step of subjecting the dehydrated azeotropic mixture to low-boiling distillation to extract a bottom product containing isopropyl alcohol may be interposed between the dehydration step and the high-boiling distillation step. Hereinafter, each additional purification step will be described.

[0050]

(Azeotropic Mixture Generation Step)

In the azeotropic mixture generation step, the purified IPA aqueous solution is supplied to the raw material supply stage of the distillation column to perform distillation, and the azeotropic mixture of IPA and water is extracted from the column top of the distillation column as a distillate, and a bottom product containing a high-boiling impurity having a boiling point higher than that of IPA is extracted from the column bottom of the distillation column.

[0051]

Specifically, since an azeotropic temperature of IPA and water is 80.1°C, by distilling the purified IPA aqueous solution at 80.1°C, the azeotropic mixture of IPA and water is extracted from the column top. On the other hand, the bottom product containing a high-boiling impurity is extracted from the column bottom. A part of the water in the bottom product may be used as water for adjusting the content of water in the liquid phase in the raw material supply stage of the low-boiling distillation step. As a result, in addition to reducing the usage amount of water and the waste water treatment cost, energy can be reduced by using the bottom product without cooling.

[0052]

In addition, the azeotropic mixture generation step may be performed according to conditions described in the low-boiling distillation step.

[0053]

(Dehydration Step)

In the dehydration step, the azeotropic mixture of IPA and water obtained in the azeotropic mixture generation step is dehydrated.

[0054]

The dehydration method is not particularly limited, and examples thereof include azeotropic distillation, adsorption, and membrane permeation. In a case where the azeotropic mixture of IPA and water is subjected to azeotropic distillation, water can be removed by adding an azeotropic

agent to perform distillation. Examples of the azeotropic agent include diethyl ether, benzene, toluene, trichloroethylene, dichloromethane, and hexenes.

[0055]

(Second Low-boiling Distillation Step)

In the second low-boiling distillation step, the azeotropic mixture dehydrated in the dehydration step is subjected to low-boiling distillation again. That is, the second low-boiling distillation step is a step of extracting a distillate containing a low-boiling impurity from the column top of the low-boiling distillation column and extracting, from the column bottom of the low-boiling distillation column, a bottom product containing IPA in which the low-boiling impurity is further reduced, and may be performed according to a desired purity of IPA.

[0056]

(High-boiling Distillation Step)

In the high-boiling distillation step, the azeotropic mixture dehydrated in the dehydration step is subjected to high-boiling distillation, a bottom product containing a high-boiling impurity is extracted from the column bottom of the high-boiling distillation column, and a distillate containing IPA in which the high-boiling impurity is further reduced is extracted from the column top of the high-boiling distillation column.

[0057]

(Other Steps)

If necessary, the distillate obtained in the high-boiling distillation step may be further subjected to a purification treatment by a method such as adsorption. In addition, particles (for example, metal particles, inorganic particles, and organic particles) may be removed by filter filtration, or ions (for example, metal ions) may be removed by an ion exchange resin.

[0058]

(Purification Degree of Purified IPA)

According to the method for producing purified IPA in which the purified IPA aqueous solution is dehydrated and subjected to additional purification as necessary as described above, it is possible to set the content of water to preferably 100 ppm by mass or less, and more preferably 1 ppm by mass to 50 ppm by mass by performing the dehydration step. Further, if the high-boiling distillation step is performed, high-boiling impurities other than toluene can also be reduced to a high degree. Therefore, it is possible to obtain purified IPA having a purity of preferably 99.9% by mass or more, and more preferably 99.99% by mass to 99.999999% by mass (provided that the content of water is excluded).

[0059]

Although embodiments of the present invention have been described above, the present invention is not limited to the above embodiments, and the above embodiments may be appropriately modified within the scope of the gist of the present invention.

EXAMPLES

[0060]

Hereinafter, examples of the present invention will be described, but the present invention is not limited to the examples. In the present examples, % and ppm are mass basis unless otherwise specified.

[0061]

<Analysis Example 1>

(Method for Measuring Water Content)

Instrument: Karl Fischer moisture meter CA-200

(manufactured by Mitsubishi Chemical Analytech Co., Ltd.)

A sample having a water content of more than 1% was diluted with IPA, and then measured. The water content in IPA used for dilution was measured in advance and confirmed to be 30 ppm. A sample having a water content of 1% or less was analyzed without being diluted. In a case where the amount of moisture is larger than expected, it takes time to perform the measurement, but the measurement value is not affected. The water content in IPA used for dilution is measured by collecting 5 g or more of a measurement sample in a glove box having a dew point of -60°C or lower using a TERUMO syringe, and the present analysis method can quantify the water content as long as the water content is 1 ppm or more.

[0062]

<Analysis Example 2>

(Method for Measuring Content of 1-methoxy-2-propanol)

After 1 L of IPA was concentrated to 1 ml by an evaporator (water bath: 80°C, 10 kPa (absolute pressure)), analysis was performed by GC/MS. As a result of calculating a quantitative lower limit using a standard substance, the quantitative lower limit of 1-methoxy-2-propanol was 0.01 ppb.

-Measurement Conditions-

Device: 7890A/5975C (manufactured by Agilent Technologies)

Analytical column: SUPELCO WAX-10 (60 m × 0.25 mm, 0.25 µm)

Column temperature: 35°C (held for 2 minutes) -> heating at 5°C/min -> 100°C -> heating at 10°C/min -> 240°C (held for 6 minutes)

Carrier gas: helium

Carrier gas flow rate: 2 mL/min

Injection port temperature: 240°C

Injection amount: 5 µl

Sample injection method: pulsed splitless method

Injection pulse pressure: 90 psi (2 minutes)

Split vent flow rate: 50 mL/min (2 minutes)

Use of gas saver: 20 mL/min (5 minutes)

Transfer line temperature: 240°C

Ion source temperature, quadrupole temperature: 230°C, 150°C

Scanning ion: m/Z = 25 to 250

SIM (selected ion detection): 75 (1-methoxy-2-propanol)

[0063]

<Analysis Example 3>

(Method for Measuring Respective Contents of Toluene and Isopropyl Acetate)

A: case where the water content in IPA is 1% or more
After the water content in IPA was adjusted to 95%, the respective contents of toluene and isopropyl acetate were analyzed by headspace gas chromatography mass spectrometry (HS/GC/MS). In the method, a detection lower limit in IPA having a water content of 5% (IPA 95%) was 0.1 ppb of toluene and 0.1 ppb of isopropyl acetate. A value of SIM can be optionally set for each compound to be quantified.

[0064]

-Measurement Conditions-

Devices: gas chromatography mass spectrometers (GC/MS)
8890 and 5977B (manufactured by Agilent Technologies),
headspace sampler 8697 (manufactured by Agilent Technologies)
Injection mode: splitless
Carrier: helium
Column: DB-1, manufactured by J&W Scientific (length: 60 m,
inner diameter: 0.32 mm, thickness: 5 μ m)
Column temperature: maintained at 30°C for 15 minutes, then
heated to 250°C at 20°C/min, and further maintained at 250°C
for 10 minutes
Column flow rate: 1.4 ml/min
Injection port pressure: 8.4 psi
Injection port temperature: 200°C
Injection amount: 1 mL (vial gas phase portion in headspace
method)
Ion source temperature: 230°C
Quadrupole temperature: 150°C

SIM (selected ion detection): 61 (isopropyl acetate), 91
(toluene)

Solvent heating temperature (headspace): 60°C

Solvent heating time (headspace): 15 minutes

[0065]

B: case of water content in IPA less than 1%

The respective contents of toluene and isopropyl acetate were analyzed by gas chromatography mass spectrometry (GC/MS). A detection lower limit in the method was 1 ppb of toluene and 1 ppb by mass of isopropyl acetate.

[0066]

A value of SIM can be optionally set for each compound to be quantified. Since toluene and isopropyl acetate are azeotropic with IPA, it is difficult to reduce the detection lower limit by a normal pressure concentration method. By using an adsorbent that easily adsorbs a substance of low polarity such as activated carbon, the detection lower limit can be set to 1 ppt or less.

[0067]

-Measurement Conditions-

Device: gas chromatography mass spectrometers (GC/MS)
8890 and 5977B (manufactured by Agilent Technologies)

Injection mode: splitless

Carrier: helium

Column: DB-1, manufactured by J&W Scientific (length: 60 m,
inner diameter: 0.32 mm, thickness: 5 µm)

Column temperature: maintained at 30°C for 15 minutes, then

heated to 250°C at 20°C/min, and further maintained at 250°C for 10 minutes

Column flow rate: 1.4 ml/min

Injection port pressure: 8.4 psi

Injection port temperature: 200°C

Injection amount: 5 µL

Ion source temperature: 230°C

Quadrupole temperature: 150°C

SIM (selected ion detection): 59 (2-methyl-2-propanol), 61 (isopropyl acetate), 91 (toluene)

[0068]

<Example 1>

(Low-boiling Distillation Step)

The low-water-content IPA waste liquid recovered from the semiconductor manufacturing device including the rinsing unit for semiconductor substrates and collected in the waste liquid receiving tank 1 for three days was purified by the low-boiling distillation step illustrated in Fig. 1. In the low-water-content IPA waste liquid, the content of water was 20% by mass (content of IPA was 80%) based on mass, and the content of toluene was 100 ppm in terms of mass ratio relative to IPA. Water was supplied to the waste liquid receiving tank 1 such that the content of water was 90% (content of IPA was 10%) with respect to the low-water-content IPA waste liquid to obtain a water content adjusting liquid to be supplied to the low-boiling distillation step.

[0069]

As the low-boiling distillation column 2 for distilling the water content adjusting liquid, an Oldershaw type low-boiling distillation column having 15 trays was installed, and it was experimentally confirmed that the number theoretical stages of the low-boiling distillation column 2 was 10. Here, the low-boiling distillation column 2 is a container having a column bottom of 2 L, the condenser 5 is installed at the column top, and a part of the distillate condensed by the condenser 5 is refluxed to the column top of the low-boiling distillation column 2. The water content adjusting liquid was supplied to the column top of the low-boiling distillation column 2 at 10 L/h to perform distillation. In this case, the temperature of the column top was 75°C to 85°C, and the pressure (gauge pressure) of the column top was 0 kPaG to 10 kPaG. In addition, the reflux volume was set to 10 L/h, a reflux ratio was set to about 1,000, and the distillate was extracted from the distillate discharge pipe 6 at 10 ml/h. Further, the bottom product (purified IPA aqueous solution) was extracted from the bottom product discharge pipe 7 at about 10 L/h such that the liquid amount at the column bottom was maintained at about 1.5 L.

[0070]

When the content of toluene in the purified IPA aqueous solution was measured, the content of toluene was 0.2 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit, and it was confirmed that the content of toluene was significantly

reduced by the low-boiling distillation step. In addition, the content of isopropyl acetate in the purified IPA aqueous solution was 1 ppb or less in terms of mass ratio relative to IPA.

[0071]

(Additional Purification Step)

The purified IPA aqueous solution obtained in the low-boiling distillation step was supplied to the raw material supply stage of the distillation column to be subjected to the azeotropic mixture generation step. That is, the bottom product (purified IPA aqueous solution) extracted from the bottom product discharge pipe 7 was supplied to the raw material supply stage of the distillation column to perform distillation, and an azeotropic mixture of IPA and water (mass ratio: 87.5:12.5) was extracted from the column top.

[0072]

Next, the azeotropic mixture of IPA and water was subjected to the dehydration step, and benzene was used as an azeotropic agent (entrainer) to extract a bottom product containing IPA in which the water content was reduced to 100 ppm or less from the column bottom. Thereafter, the bottom product containing IPA was subjected to the second low-boiling distillation step, a bottom product containing IPA in which low-boiling impurities were further reduced was extracted, then the bottom product containing IPA was subjected to the high-boiling distillation step, and a distillate containing IPA in which high-boiling impurities were further reduced was

extracted, and cooled. The distillate containing IPA was made to pass through the ion exchange resin, and then pass through three types of filters (fluororesin filters having hole diameters of 50 nm, 10 nm, and 2 nm) to obtain purified IPA.

[0073]

The content of toluene in the purified IPA was 0.1 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit. In addition, the contents of isopropyl acetate and 1-methoxy-2-propanol are also shown in Table 1.

[0074]

<Comparative Example 1>

(Low-boiling Distillation Step)

A low-boiling distillation step was performed in the same manner as in Example 1 except that water was supplied to the waste liquid receiving tank 1 such that the content of water was 50% (content of IPA was 50%) with respect to the low-water-content IPA waste liquid accommodated in the waste liquid receiving tank 1 to obtain a water content adjusting liquid. When the content of toluene in the purified IPA aqueous solution extracted from the bottom product discharge pipe 7 was measured, the content of toluene was 8 ppb in terms of mass ratio relative to IPA. In addition, the content of isopropyl acetate in the purified IPA aqueous solution was 175 ppb in terms of mass ratio relative to IPA.

[0075]

(Additional Purification Step)

An additional purification step was performed in the same manner as in Example 1 except that the purified IPA aqueous solution obtained by the low-boiling distillation step was used. The content of toluene in the purified IPA thus obtained was 6 ppb in terms of mass ratio relative to IPA. In addition, contents of isopropyl acetate and 1-methoxy-2-propanol are also shown in Table 1.

[0076]

<Comparative Example 2>

(Low-boiling Distillation Step)

A low-boiling distillation step was performed in the same manner as in Example 1 except that water was not supplied to the low-water-content IPA waste liquid accommodated in the waste liquid receiving tank 1, and the low-water-content IPA waste liquid was used instead of the water content adjusting liquid. When the content of toluene in the purified IPA aqueous solution extracted from the bottom product discharge pipe 7 was measured, the content of toluene was 12,400 ppb in terms of mass ratio relative to IPA. In addition, the content of isopropyl acetate in the purified IPA aqueous solution was 6,950 ppb in terms of mass ratio relative to IPA.

[0077]

(Additional Purification Step)

An additional purification step was performed in the same manner as in Example 1 except that the purified IPA aqueous solution obtained by the low-boiling distillation step was used. The content of toluene in the purified IPA thus obtained

was 100 ppb in terms of mass ratio relative to IPA. In addition, the contents of isopropyl acetate and 1-methoxy-2-propanol are also shown in Table 1.

[0078]

<Example 2>

(Low-boiling Distillation Step)

A low-boiling distillation step was performed in the same manner as in Example 1 except that water was supplied to the waste liquid receiving tank 1 such that the content of water was 70% (content of IPA was 30%) with respect to the low-water-content IPA waste liquid accommodated in the waste liquid receiving tank 1 to obtain a water content adjusting liquid. When the content of toluene in the purified IPA aqueous solution extracted from the bottom product discharge pipe 7 was measured, the content of toluene was 0.2 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit, and it was confirmed that the content of toluene was significantly reduced by the low-boiling distillation step. In addition, the content of isopropyl acetate in the purified IPA aqueous solution was 1.2 ppb in terms of mass ratio relative to IPA.

[0079]

(Additional Purification Step)

An additional purification step was performed in the same manner as in Example 1 except that the purified IPA aqueous solution obtained by the low-boiling distillation step was used. The content of toluene in the purified IPA thus obtained

was 0.1 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit. In addition, the content of 1-methoxy-2-propanol is also shown in Table 1.

[0080]

<Example 3>

(Low-boiling Distillation Step)

A low-boiling distillation step was performed in the same manner as in Example 1 except that water was supplied to the waste liquid receiving tank 1 such that the content of water was 80% (content of IPA was 20%) with respect to the low-water-content IPA waste liquid accommodated in the waste liquid receiving tank 1 to obtain a water content adjusting liquid. When the content of toluene in the purified IPA aqueous solution extracted from the bottom product discharge pipe 7 was measured, the content of toluene was 0.2 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit, and it was confirmed that the content of toluene was significantly reduced by the low-boiling distillation step. In addition, the content of isopropyl acetate in the purified IPA aqueous solution was 1 ppb or less in terms of mass ratio relative to IPA.

[0081]

(Additional Purification Step)

An additional purification step was performed in the same manner as in Example 1 except that the purified IPA aqueous

solution obtained by the low-boiling distillation step was used. The content of toluene in the purified IPA thus obtained was 0.1 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit. In addition, the contents of isopropyl acetate and 1-methoxy-2-propanol are also shown in Table 1.

[0082]

<Example 4>

(Low-boiling Distillation Step)

A low-boiling distillation step was performed in the same manner as in Example 1 except that an Oldershaw type low-boiling distillation column having 60 trays was used as the low-boiling distillation column 2. It was experimentally confirmed that the number of theoretical stages of the low-boiling distillation column 2 was 40. When the content of toluene in the purified IPA aqueous solution extracted from the bottom product discharge pipe 7 was measured, the content of toluene was 0.2 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit, and it was confirmed that the content of toluene was significantly reduced by the low-boiling distillation step. In addition, the content of isopropyl acetate in the purified IPA aqueous solution was 1 ppb or less in terms of mass ratio relative to IPA.

[0083]

(Additional Purification Step)

An additional purification step was performed in the same

manner as in Example 1 except that the purified IPA aqueous solution obtained by the low-boiling distillation step was used. The content of toluene in the purified IPA thus obtained was 0.1 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit. In addition, the contents of isopropyl acetate and 1-methoxy-2-propanol are also shown in Table 1.

[0084]

<Example 5>

(Low-boiling Distillation Step)

A low-boiling distillation step was performed in the same manner as in Example 4 except that a low-water-content IPA waste liquid in which the content of water was 20% (content of IPA was 80%) based on mass and the content of toluene was 500 ppm in terms of mass ratio relative to IPA was used. When the content of toluene in the purified IPA aqueous solution extracted from the bottom product discharge pipe 7 was measured, the content of toluene was 0.2 ppb or less in terms of mass ratio relative to IPA, which was equal to or less than the detection lower limit, and it was confirmed that the content of toluene was significantly reduced by the low-boiling distillation step. In addition, the content of isopropyl acetate in the purified IPA aqueous solution was 1 ppb or less in terms of mass ratio relative to IPA.

[0085]

(Additional Purification Step)

An additional purification step was performed in the same

manner as in Example 1 except that the purified IPA aqueous solution obtained by the low-boiling distillation step was used. The content of toluene in the purified IPA thus obtained was 0.1 ppb or less, which was equal to or less than the detection lower limit. In addition, the contents of isopropyl acetate and 1-methoxy-2-propanol are also shown in Table 1.

[0086]

[Table 1]

	Low-water-content IPA waste liquid				Water content adjusting liquid	Low-boiling distillation column			Purified IPA aqueous solution		Purified IPA		
	Content of water (%)	Content of toluene (ppm)	Content of isopropyl acetate (ppm)	Content of 1-methoxy-2-propanol (ppm)		Number of stages	Supply stage	Number of theoretical stages	Content of toluene (ppb)	Content of isopropyl acetate (ppb)	Content of toluene (ppb)	Content of isopropyl acetate (ppb)	Content of 1-methoxy-2-propanol (ppb)
Example 1	20	100	10	150	90	15	Column top	10	<0.2	<1	<0.1	<1	<1
Comparative Example 1	20	100	10	150	50	15	Column top	10	8	175	6	90	<1
Comparative Example 2	20	100	10	150	—	15	Column top	10	12400	6950	9240	3510	<1
Example 2	20	100	10	150	70	15	Column top	10	<0.2	1.2	<0.1	<1	<1
Example 3	20	100	10	150	80	15	Column top	10	<0.2	<1	<0.1	<1	<1
Example 4	20	100	10	150	90	60	Column top	40	<0.2	<1	<0.1	<1	<1
Example 5	20	500	20	300	90	60	Column top	40	<0.2	<1	<0.1	<1	<1

In Table 1, the contents of toluene, isopropyl acetate, and 1-methoxy-2-propanol are in terms of mass ratio relative to IPA.
[0087]

As can be seen from Table 1, in Examples 1 to 5, toluene is removed to a high degree from the low-water-content IPA waste liquid, and the purified IPA aqueous solution and the purified IPA have high purity. In contrast, in Comparative Example 1, since the content of water in the water content adjusting liquid is 50% by mass, toluene is not removed to a high degree from the low-water-content IPA waste liquid, and the purified IPA aqueous solution and the purified IPA have low purity. In addition, in Comparative Example 2, since water was not supplied to the low-water-content IPA waste liquid and the content of water was not adjusted, toluene is not removed to a high degree from the low-water-content IPA waste liquid, and the purified IPA aqueous solution and the purified IPA have low purity.

EXPLANATION OF REFERENCE NUMERALS

[0088]

- 1: waste liquid receiving tank
- 2: low-boiling distillation column
- 3: waste liquid supply pipe
- 4: distillation target liquid supply pipe
- 5: condenser
- 6: distillate discharge pipe
- 7: bottom product discharge pipe

8: water supply pipe

CLAIMS

[Claim 1]

A method for producing a purified isopropyl alcohol aqueous solution from a low-water-content isopropyl alcohol waste liquid containing toluene as an impurity, the method comprising:

a low-boiling distillation step of supplying the low-water-content isopropyl alcohol waste liquid to a raw material supply stage of a distillation column, extracting a distillate containing toluene from a column top of the distillation column, and extracting a bottom product containing isopropyl alcohol and water from a column bottom of the distillation column,

wherein a content of water in a liquid phase in the raw material supply stage of the distillation column is adjusted to 70% by mass or more and 95% by mass or less.

[Claim 2]

The method for producing a purified isopropyl alcohol aqueous solution according to claim 1, wherein the low-water-content isopropyl alcohol waste liquid is a waste liquid recovered from a semiconductor manufacturing device including a rinsing unit for semiconductor substrates.

[Claim 3]

The method for producing a purified isopropyl alcohol

aqueous solution according to claim 1 or 2, wherein the content of water in the liquid phase in the raw material supply stage of the distillation column is adjusted to 80% by mass or more and 93% by mass or less.

[Claim 4]

The method for producing a purified isopropyl alcohol aqueous solution according to claim 1 or 2, wherein a content of toluene in the low-water-content isopropyl alcohol waste liquid is 1 ppm or more and 2,000 ppm or less in terms of mass ratio relative to isopropyl alcohol.

[Claim 5]

A method for producing purified isopropyl alcohol from a purified isopropyl alcohol aqueous solution obtained by the method for producing a purified isopropyl alcohol aqueous solution according to claim 1 or 2, the method comprising:

a dehydration step of dehydrating the purified isopropyl alcohol aqueous solution.

[Claim 6]

The method for producing purified isopropyl alcohol according to claim 5, further comprising: an azeotropic mixture generation step of distilling the purified isopropyl alcohol aqueous solution and extracting an azeotropic mixture of isopropyl alcohol and water as a distillate; and

a dehydration step of adding an azeotropic agent to the

azeotropic mixture of isopropyl alcohol and water to perform distillation, and extracting a bottom product containing isopropyl alcohol to perform dehydration.

[Claim 7]

The method for producing purified isopropyl alcohol according to claim 5, wherein the purified isopropyl alcohol is a semiconductor chemical liquid.

[Claim 8]

The method for producing purified isopropyl alcohol according to claim 7, wherein the semiconductor chemical liquid is a rinsing liquid for semiconductor substrates.

[Claim 9]

The method for producing purified isopropyl alcohol according to claim 6, further comprising: a second low-boiling distillation step of subjecting the azeotropic mixture which has been dehydrated to low-boiling distillation to extract a bottom product containing isopropyl alcohol; and

a high-boiling distillation step of subjecting the bottom product containing isopropyl alcohol to high-boiling distillation to extract a distillate containing isopropyl alcohol.