

DESCRIPTION

Title of the Invention: METHOD FOR PRODUCING PURIFIED
ISOPROPYL ALCOHOL

TECHNICAL FIELD

[0001]

The present invention relates to a method for producing purified isopropyl alcohol from crude isopropyl alcohol containing butyl formate as an impurity.

BACKGROUND ART

[0002]

Isopropyl alcohol (hereinafter, also abbreviated as "IPA") is miscible with both water and organic solvents, and is widely used as a solvent for paints, a solvent for inks, and a raw material for various synthesis. Further, high-purity IPA has also been used in considerable quantity in a rinsing unit for semiconductor substrates in semiconductor manufacturing equipment, and the amount of high-purity IPA to be used is expected to increase in the future. Known methods for purifying crude IPA to produce high-purity IPA include purification through distillation (see, Nonpatent Document 1).

[0003]

The high-purity IPA has a high manufacturing cost, and therefore the rinsing unit for semiconductor substrates where the high-purity IPA is used in large amounts, may contribute

to an increase in cost of manufacturing semiconductors. In addition, IPA waste liquids collected after use in the rinsing unit for semiconductor substrates are usually subjected to a combustion treatment, during which carbon dioxide, which is thought to contribute to global warming, is emitted, and a reduction of the amount of the IPA waste liquid to be disposed of has also been desired from the viewpoint of environment conservation. For these reasons, there is a growing demand for purifying and reusing the IPA waste liquid (see, for example, Patent Document 1).

[0004]

Incidentally, a rinsing unit for semiconductor substrates is generally provided downstream of and adjacent to a cleaning unit for semiconductor substrates. Since ultrapure water or a liquid of high water content is typically used as a cleaning liquid in the cleaning unit for semiconductor substrates, an operation of removing moisture attached to the surface of the semiconductor substrate when in the cleaning unit for semiconductor substrates is performed in the rinsing unit for semiconductor substrates. Accordingly, IPA waste liquids collected from the rinsing unit for semiconductor substrates are liquids of low water content. In addition, IPA is also used in large amounts in a developing unit and a pre-wetting unit in the semiconductor manufacturing equipment, and further, water is also frequently used in the semiconductor manufacturing equipment for various purposes. Thus, water-containing IPA waste liquids are discharged from semiconductor

manufacturing equipment including the rinsing unit for semiconductor substrates. For example, Patent Document 2 assumes that the water contents of the water-containing IPA waste liquids are about 5% by mass. For example, Patent Document 3 proposes purification of a water-containing IPA waste liquid having a water content of 5 to 15% through distillation, as a method for recovering IPA from such water-containing IPA waste liquids.

Citation List

Patent Documents

[0005]

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 Unexamined Patent Application, Publication No. 112999679

Non-Patent Documents

[0006]

Non-Patent Document 1: Yuuki Gousei Kagaku (Journal of Synthetic Organic Chemistry, Japan), vol. 35, No. 9, 1977, pages 762-766

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0007]

On the other hand, various compounds other than IPA are

used in the semiconductor manufacturing equipment, e.g., the cleaning unit and the rinsing unit. Examples of the various compounds other than IPA include solvent components for photoresist materials used in the developing unit, and solvent components for adhesives used for various purposes. Accordingly, IPA waste liquids discharged from the semiconductor manufacturing equipment via the cleaning unit and the rinsing unit contain these solvent components in addition to water.

[0008]

The present inventors have studied the purification of the IPA waste liquids and the production of high-purity IPA that can be supplied to semiconductor manufacturing equipment, and consequently found that solvent components difficult to be removed from the IPA waste liquids include butyl formate. It is therefore an object of the present invention to provide a method for producing purified IPA with high purity from crude IPA containing butyl formate as an impurity.

Means for Solving the Problems

[0009]

In view of the above problems, the present inventors have studied separation and removal of butyl formate by the purification of crude IPA through distillation, and consequently found the difficulty in the production of purified IPA. Specifically, crude IPA contains no water but contains butyl formate, an azeotropic mixture of butyl formate and IPA is obtained, and therefore the separation and removal

of butyl formate through distillation under non-high-pressure conditions is difficult. On the other hand, when crude IPA contains water and butyl formate, distillation under non-high-pressure conditions allows for separation and removal of butyl formate as a low-boiling-point impurity. However, an azeotropic mixture of IPA and water is obtained, causing a need of azeotropic distillation, and rendering the production of purified IPA cumbersome. Furthermore, it has also been found that when the crude IPA further contains formic acid or 1-butanol, dehydration of the crude IPA caused re-generation of butyl formate.

[0010]

Based on the findings described above, a method for producing purified IPA in the case where the crude IPA contains butyl formate but no water has been examined, and consequently it has been found that high-pressure distillation of crude IPA enabled purified IPA to be obtained as a distillate from the top of a distillation column with butyl formate being highly removed, to accomplish the present invention.

[0011]

More specifically, an aspect of the present invention relates to a method for producing purified isopropyl alcohol from crude isopropyl alcohol containing butyl formate as an impurity, the method including a high-pressure distillation step of subjecting the crude isopropyl alcohol to high-pressure distillation. In the aspect of the present invention,

the following embodiments are preferred.

[0012]

(1) The proportion of butyl formate to isopropyl alcohol in the crude isopropyl alcohol is 10 ppb by mass or more and 100000 ppb by mass or less.

(2) The crude isopropyl alcohol is subjected to high-pressure distillation under conditions of an absolute pressure of 120 kPa or higher and 1000 kPa or lower.

(3) The method further includes a dehydration step of dehydrating a crude isopropyl alcohol feedstock solution containing a formate ion, 1-butanol, and water to obtain the crude isopropyl alcohol.

(4) The proportion of the formate ion to isopropyl alcohol in the crude isopropyl alcohol feedstock solution is 10 ppb by mass or more and 100000 ppb by mass or less.

(5) The proportion of 1-butanol to isopropyl alcohol in the crude isopropyl alcohol feedstock solution is 10 ppb by mass or more and 100000 ppb by mass or less.

(6) The crude isopropyl alcohol feedstock solution is a waste liquid collected from semiconductor manufacturing equipment.

Effects of the Invention

[0013]

According to the present invention, purified IPA with high purity can be produced from crude IPA containing butyl formate as an impurity. Therefore, an IPA waste liquid collected from semiconductor manufacturing equipment including a rinsing unit for semiconductor substrates, or the like can

be easily recycled into high-purity IPA, and the high-purity IPA can be used as a chemical solution for semiconductors, in particular, a rinsing liquid for semiconductor substrates, and thus has extremely high industrial value.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

[FIG. 1A] FIG. 1A is an overall graph illustrating the mol fractions of liquid phase IPA and gas phase IPA for each pressure;

[FIG. 1B] FIG. 1B is an enlarged view of a high mol fraction region of the graph illustrating the mol fractions of liquid phase IPA and gas phase IPA for each pressure; and

[FIG. 2] FIG. 2 is a schematic diagram illustrating a distillation column for low-boiling-point materials used in Example 6.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0015]

The method for producing purified IPA according to the present embodiment is a method for producing purified IPA from crude IPA containing butyl formate as an impurity, the method including a high-pressure distillation step of subjecting the crude IPA to high-pressure distillation. Although the details of the reason why the method for producing purified IPA according to the present embodiment enables butyl formate in the crude IPA containing butyl formate as an impurity to be

removed to a higher degree are unclear, the present inventors speculate as follows. As described above, an IPA waste liquid discharged from semiconductor manufacturing equipment may contain water and butyl formate. In this case, butyl formate can be separated and removed by distillation under non-high-pressure conditions. On the other hand, when the IPA waste liquid contains no water, butyl formate is impossible to be separated and removed by distillation under non-high-pressure conditions, since an azeotropic mixture of butyl formate and IPA is formed. On the other hand, at or above the boiling point of IPA, in particular at 100°C or higher, a difference in saturated vapor pressure between IPA and butyl formate is large, which renders the formation of the azeotropic mixture of butyl formate and IPA less likely. Thus, it is presumed that distillation under high-pressure conditions does not lead to an azeotropic mixture of butyl formate and IPA, and butyl formate can be separated and removed.

[0016]

In this specification, the expression "A to B" in regard to numerical values A and B is intended to mean "A or more and B or less", unless otherwise specified. In addition, in such an expression, when only the numerical value B is accompanied by a unit, the unit shall also apply to the numerical value A. In the following description, "ppm", "ppb", and "ppt" representing the concentration are each on mass basis, including in Examples, unless otherwise specified. Hereinafter, the method for producing purified IPA according

to the present embodiment will be described in detail.

[0017]

<Crude IPA>

In the method for producing purified IPA according to the present embodiment, crude IPA containing butyl formate as an impurity is subjected to high-pressure distillation. Butyl formate has a boiling point of about 106°C at normal pressure. The crude IPA is not limited, and may be a reaction product obtained by reacting propylene with water by a propylene method, a reaction product obtained by reducing acetone, or an IPA waste liquid.

[0018]

The proportion of butyl formate to isopropyl alcohol in the crude IPA is not limited, and is preferably 10 to 100000 ppb, and more preferably 100 to 10000 ppb. When the proportion of butyl formate to isopropyl alcohol in the crude IPA is within the above range, the effect of separating and removing butyl formate in the present embodiment is remarkably exhibited. On the other hand, even when the proportion of butyl formate to isopropyl alcohol in the crude IPA exceeds 100000 ppb, butyl formate can be removed by adjusting the conditions of the high-pressure distillation, as described later.

[0019]

The crude IPA may contain other components (for example, water, acetone, and/or 1-propanol). In such a case, when the content of IPA in the crude IPA is low, the production of the

purified IPA requires many steps and is not efficient, and the efficiency of separation and removal of butyl formate tends to decrease. Accordingly, the content of IPA in the crude IPA is preferably 95% or more, and more preferably 99% or more. When the content of IPA in the crude IPA is low, it is preferable to remove the impurities by a known procedure before subjecting the crude IPA to the method for producing purified IPA according to the present embodiment. The content of IPA in the crude IPA can be determined by gas chromatography.

[0020]

Further, the crude IPA may contain water. However, in a case where the crude IPA contains a large amount of water, the efficiency of separation and removal of butyl formate tends to decrease. Thus, the method for producing purified IPA according to the present embodiment may further include a dehydration step of dehydrating a water-containing crude IPA feedstock solution to obtain crude IPA. Therefore, the content of water in the crude IPA is preferably 1000 ppm or less, more preferably 100 ppm or less, and still more preferably 1 to 50 ppm. Examples of the method for dehydrating a water-containing crude IPA feedstock solution include distillation, adsorption, membrane permeation, etc. The content of water in the crude IPA can be determined by the Karl Fischer method.

[0021]

<Method for Preparing Crude IPA>

The crude IPA feedstock solution is not limited. Hereinafter, a method of preparing the crude IPA in the case

of using the IPA waste liquid as the crude IPA feedstock solution will be described in detail. Note that a solution obtained by diluting the IPA waste liquid with water may be employed as the crude IPA feedstock solution.

[0022]

<IPA Waste Liquid>

An IPA waste liquid is often discharged from various industrial facilities where paints and/or inks are produced, used, or the like, and liquids collected from these facilities may also be applied to the present method without any limitation; most suitable is a waste liquid collected from semiconductor manufacturing equipment including a rinsing unit for semiconductor substrates. In particular, the waste liquid collected from the rinsing unit for semiconductor substrates tends to have a composition suitable for producing purified IPA, and is suitably applied. In addition, the IPA waste liquid may contain a developing solution, a pre-wetting liquid, an etching liquid, a cleaning liquid, a stripping liquid, a drying liquid, or the like discharged from semiconductor manufacturing equipment.

[0023]

The content of IPA in the IPA waste liquid is preferably 5% by mass or more and 95% by mass or less, more preferably 10 to 80% by mass, and particularly preferably 15 to 30% by mass. On the other hand, the content of water in the IPA waste liquid is preferably less than 95% by mass, more preferably 20 to 90% by mass, and particularly preferably 70 to 85% by mass.

A higher content of water in the IPA waste liquid tends to lead to a huge facility, and increase transportation costs.

[0024]

The IPA waste liquid may contain a formate ion, butyl formate, and 1-butanol. The proportion of the total amount of the formate ion, butyl formate, and 1-butanol to IPA in the IPA waste liquid is preferably 100 to 1000000 ppb, more preferably 1000 to 100000 ppm. When the proportion of the total amount of the formate ion, butyl formate, and 1-butanol to IPA in the IPA waste liquid is within the above range, the effect of separating and removing butyl formate is remarkably exhibited. Causes of contamination by butyl formate and 1-butanol are considered to be, for example, their use in a step prior to a semiconductor cleaning step, and their entry as impurities in butyl acetate. In addition, causes of contamination by the formate ion are considered to be, for example, its use in a step prior to the semiconductor cleaning step, and its entry as an impurity in acetic acid and methanol. Further, the IPA waste liquid is usually uncontrolled in terms of entry of air, and oxygen in the air may cause the formation of formic acid. The contact of IPA with air is known to produce formic acid, and in particular, formic acid is easily produced in the presence of water.

[0025]

The IPA waste liquid may further contain a low-boiling-point impurity having a lower boiling point than IPA, including: olefins such as butene, pentene, and hexene;

alkanes such as butane, pentane, and hexane; aldehydes such as formaldehyde, acetaldehyde, and propylene aldehyde; ketones such as acetone and butanone; alcohols such as methanol, ethanol, and 2-methyl-2-propanol; chloroalkanes such as dichloromethane, chloroform, carbon tetrachloride, and vinyl chloride; and silylated alcohols such as trimethylsilylated IPA and trimethylsilylated ethanol. The proportion of the total amount of the low-boiling-point impurities to IPA in the IPA waste liquid is preferably 0.1 to 10000 ppm, and more preferably 1 to 100 ppm.

[0026]

Furthermore, the IPA waste liquid may further contain a high-boiling-point impurity having a higher boiling point than IPA. Specifically, when the IPA waste liquid is a waste liquid of a chemical solution for semiconductors, in particular, a waste liquid of a cleaning liquid or a waste liquid of a drying liquid, the IPA waste liquid often further contains a high-boiling-point impurity, including: 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 a nitrate ion, a nitrite ion, a sulfate ion, a chloride ion, a fluoride ion or the like as an anion; aldehyde and ketones such as crotonaldehyde and 2-pentanone; alcohols such as 1-propanol, 2-butanol, and 1-butanol; ethers such as 1-methoxy-2-propanol, 1-(2-methoxypropoxy)propan-2-ol, and 1-(2-methoxy-2-methylethoxy)-2-propanol; aromatics such as toluene and

xylenes (ortho, meta, and para); alkanes such as octane, decane, and hexadecane; carboxylic acid esters such as isopropyl acetate and isopropyl propionate; phthalic acid esters such as dioctyl phthalate and dibutyl phthalate; and adipic acid esters such as dioctyl adipate.

[0027]

<Method for Dehydrating IPA Waste Liquid>

For an IPA waste liquid containing a large amount of water, the IPA waste liquid is preferably dehydrated. Specifically, the IPA waste liquid is distilled, and a distillate containing an azeotropic mixture of IPA and water is taken out from the top of a distillation column for high-boiling-point materials, then the distillate is subjected to azeotropic distillation, and an IPA-containing bottom product is withdrawn to obtain crude IPA. In this procedure, the low-boiling-point impurities and a part of the high-boiling-point impurities can also be separated and removed.

[0028]

<Method for Removing Low-Boiling-Point Impurity and High-Boiling-Point Impurity in IPA Waste Liquid>

For an IPA waste liquid containing a low-boiling-point impurity and a high-boiling-point impurity, it is preferred that the IPA waste liquid is distilled and a first bottom product containing IPA and water is withdrawn, then water in the first bottom product is removed as described above and an IPA-containing second bottom product is withdrawn, and then the IPA-containing second bottom product is distilled to

obtain crude IPA as a bottom product. High-pressure distillation of the crude IPA allows for removal of the impurities to a higher degree.

[0029]

In the procedure described above, in some cases, the proportion of butyl formate to IPA in the second bottom product is higher than the proportion of butyl formate to IPA in the first bottom product. This is presumed to be due to the formation of butyl formate during the removal of water in the first bottom product. More specifically, it is presumed that when the IPA waste liquid contains a formate ion and 1-butanol, the formate ion and 1-butanol produce butyl formate by dehydrative condensation. From the viewpoint of reducing the proportion of butyl formate to IPA in the purified IPA as much as possible, the proportion of the formate ion to IPA in the IPA waste liquid is preferably 10 to 100000 ppb, and more preferably 100 to 10000 ppb. In addition, the proportion of 1-butanol to IPA in the IPA waste liquid is preferably 10 to 100000 ppb, and more preferably 100 to 10000 ppb.

[0030]

The proportion of the formate ion to IPA in the IPA waste liquid can be determined by ion chromatography. The proportions of butyl formate and 1-butanol to IPA in the IPA waste liquid can be determined by GC/MS.

[0031]

Crude IPA can be prepared by the method described above.

[0032]

<High-Pressure Distillation of Crude IPA>

In the method for producing purified IPA according to the present embodiment, the crude IPA is subjected to high-pressure distillation. Specifically, the crude IPA is distilled under high-pressure conditions in which the absolute pressure is equal to or higher than atmospheric pressure. Since butyl formate has a higher boiling point than IPA, butyl formate can be withdrawn as a bottom product so long as it does not form an azeotrope during distillation. FIGS. 1A and 1B are graphs illustrating the mol fraction of liquid phase IPA (X-axis) and gas phase IPA (Y-axis) for each pressure. Note that when the mixed liquid of IPA and butyl formate is distilled, the sum of the mol fractions is 1 because of the gas-liquid equilibrium of the two-component system. At a pressure (absolute pressure) of 101 kPa, when the mol fraction of IPA is 0.96 or more, the line overlaps with the diagonal line (a line indicating that the mol fraction of IPA in the liquid phase is equal to the mol fraction of IPA in the gas phase) (see, FIG. 1B). In other words, this indicates that the concentrations of IPA and butyl formate are the same in the liquid phase and in the gas phase. As such, at a pressure (absolute pressure) of 101 kPa, butyl formate and IPA are azeotropic, and butyl formate is difficult to separate and remove from the crude IPA.

[0033]

On the other hand, at a pressure (absolute pressure) of 200 kPa and 300 kPa (see, FIG. 1B), butyl formate and IPA are

not azeotropic, and butyl formate can be withdrawn as a bottom product during high-pressure distillation. The absolute pressure during the high-pressure distillation is preferably 120 to 1000 kPa, more preferably 150 to 800 kPa, and still more preferably 200 to 500 kPa. When the absolute pressure during the high-pressure distillation is less than 120 kPa, butyl formate cannot be sufficiently separated and removed, and when the absolute pressure exceeds 1000 kPa, the costs for facilities increase. The temperature during the high-pressure distillation may be appropriately selected depending on the boiling point of IPA at a desired absolute pressure. For example, at an absolute pressure of 200 kPa, the boiling point of IPA is about 100°C.

[0034]

The high-pressure distillation column may be either a tray column or a packed column, and is preferably a tray column. The theoretical plate number of the high-pressure distillation column is preferably 10 to 200, and more preferably 20 to 100. Examples of the tray in the tray column include a crossflow tray, a shower tray, and the like. Examples of packings in the packed column include Raschig rings, Lessing rings, and the like. Examples of the material of the column and the packings include iron, stainless steel, Hastelloy, borosilicate glass, quartz glass, fluororesin (e.g., polytetrafluoroethylene), etc.

[0035]

In the high-pressure distillation column, the number of

plates from a feed plate to the column bottom is preferably 5 or more in terms of theoretical plate number, and the number of plates from the feed plate to the column top is preferably 5 or more in terms of theoretical plate number. Note that in the calculation of the position of the feed plate, the column bottom and the column top are not included in the theoretical plates. It is preferable that the theoretical plates of the entire high-pressure distillation column are confirmed by actual operation and compositional analysis.

[0036]

Preferably, a part of the purified IPA distilled off from the top of the high-pressure distillation column is refluxed and the rest of the purified IPA is taken out as a distillate. More specifically, the reflux ratio (reflux amount/distillate amount) is preferably 1.1 or more and 100 or less, more preferably 1.2 or more and 10 or less, and still more preferably 1.5 or more and 5 or less. Adjustment of the reflux ratio, the theoretical plate number, and the absolute pressure allows for separating and removing butyl formate, while reducing the amount of IPA withdrawn from the column bottom as much as possible, to give purified IPA with butyl formate as a high-boiling-point impurity being reduced. The proportion of butyl formate to IPA in the purified IPA is preferably 100 ppb or less, more preferably 10 ppb or less, and still more preferably 0.1 ppb or less.

[0037]

In the presence of another distillation step, the high-

pressure distillation step in the method for producing purified IPA according to the present embodiment is preferably carried out as the final distillation step.

[0038]

In the high-pressure distillation step of the method for producing purified IPA according to the present embodiment, butyl formate can be removed, and additionally a high-boiling-point impurity having a higher boiling point than IPA, which is contained in the crude IPA, can be removed. The high-boiling-point impurity is not limited so long as it has a higher boiling point than IPA, and examples thereof 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 a nitrate ion, a nitrite ion, a sulfate ion, a chloride ion, a fluoride ion or the like as an anion; aldehyde and ketones having 4 to 8 carbon atoms such as 2-pentanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, butanal, 3-methylbutanal, and 3-methylpentanal; alcohols having 3 to 8 carbon atoms such as 1-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 2-methyl-3-pentanol, 3-methyl-3-pentanol, 1-methyl-2-pentanol, 1-heptanol, 2-methylhexanol, 1-octanol, and 2-methylheptanol; ethers such as 1-methoxy-2-propanol, 1-(2-methoxypropoxy)propan-2-ol, and 1-(2-methoxy-2-methylethoxy)-2-propanol; alkanes having 8 to 20 carbon atoms such as octane, decane, and hexadecane; carboxylic acid esters such as isopropyl acetate, isopropyl propionate, isopropyl formate,

and butyl formate; phthalic acid esters such as dioctyl phthalate and dibutyl phthalate; adipic acid esters such as dioctyl adipate; and the like. According to the method for producing purified IPA according to the present embodiment, the high-boiling-point impurity can also be removed to a higher degree.

[0039]

The high-boiling-point impurity withdrawn from the column bottom as described above may be discharged to the outside of the system, subjected to separation of a high concentration of impurities, and utilized in other applications, or recycled as a fuel or the like.

[0040]

<Other Steps>

The purified IPA may be further purified by adsorption or the like as necessary. For example, the purified IPA may be subjected to filtration through a filter to remove metal particles, inorganic particles, organic particles or the like, or brought into contact with an ion exchange resin or the like to remove metal ions, or the like.

EXAMPLES

[0041]

Hereinafter, examples of the present invention will be described, but the present invention is not limited to the examples. Note that in the examples, % and ppm are on a mass basis unless otherwise specified. The content of impurities in

the sample was analyzed by the following methods.

[0042]

(Method for Measuring Content of Water in Sample)

Instrument: Karl Fischer moisture meter CA-200 (from Mitsubishi Chemical Analytech Co., Ltd.) When the water content in the sample was assumed to exceed 1%, the sample was diluted with IPA and then the water content in the diluted sample was measured. The content of water in IPA used for the dilution was determined beforehand and confirmed to be 100 ppm or less. When the content of water in the sample was assumed to be 1% or less, the content of water in the sample was determined without dilution. Note that when the content of water in the sample is higher than assumed, it takes more time to complete the measurement but the measured value is not affected. In addition, when the content of water in the sample is 100 ppm or less, it is preferable to take 5 g or more of the sample with a Terumo syringe in a glove box with a dew point of -60°C or lower and measure the content of water in the sample, and this analysis method is capable of quantifying water as long as the content of water in the sample is 1 ppm or more.

[0043]

(Method for Determining Proportion of Butyl Formate to IPA in Sample)

<A: For Content of Water in Sample of 1% by Mass or More>

After the content of water in a sample was adjusted to 95% by mass, the proportion of butyl formate to IPA in the

sample was analyzed by headspace gas chromatography-mass spectrometry (HS/GC/MS). Note that this analysis method can additionally analyze 1-butanol, trimethylsilylated IPA, and the like with high sensitivity. The lower detection limits of this analysis method were 1 ppb, 1 ppb, and 1 ppb for butyl formate, 1-butanol, and trimethylsilylated IPA, respectively. The numerical value of SIM can be set as appropriate for each compound to be quantified.

[0044]

- Measurement Conditions -

Apparatus: gas chromatograph-mass spectrometer (GC/MS)
8890, 5977B (from Agilent Technologies) and headspace sampler
8697 (from Agilent Technologies)
Injection mode: splitless
Carrier: helium
Column: DB-1 (length 60 m, inner diameter 0.32 mm, thickness 5 μ m) (from J&W Scientific)
Column temperature: holding at 30°C for 15 minutes, then increase to 250°C at 20°C/min, and then holding at 250°C for 10 minutes. Column flow rate: 1.4 ml/min
Inlet pressure: 8.4 psi
Inlet temperature: 200°C
Injection volume: 1 mL (vial headspace in headspace method)
Ion source temperature: 230°C
Quadrupole temperature: 150°C
SIM (selected ion monitoring): 56 (butyl formate, 1-butanol), 117 (trimethylsilylated IPA)

Solvent heating temperature (head space): 60°C

Solvent heating time (headspace): 15 minutes

<B: For Content of Water in Sample of Less Than 1% by Mass>

The proportion of butyl formate to IPA in a sample was determined by gas chromatography mass spectrometry (GC/MS). Note that this analysis method can additionally analyze 1-butanol, trimethylsilylated IPA, and the like with high sensitivity. The lower detection limits of this analysis method were 0.1 ppb, 0.1 ppb, and 0.1 ppb for butyl formate, 1-butanol, and trimethylsilylated IPA, respectively.

[0045]

The numerical value of SIM can be set as appropriate for each compound to be quantified. Since butyl formate forms an azeotrope with IPA, it is difficult to further lower the lower detection limit by a normal pressure concentration procedure. The lower detection limit can be further lowered by concentration under high-pressure conditions, as in the method for producing purified IPA according to the present embodiment, or by using an adsorbent, such as activated carbon, that easily adsorbs a less polar substance, and the lower detection limit can be lowered to 1 ppt or less.

[0046]

- Measurement Conditions -

Apparatus: gas chromatograph-mass spectrometer (GC/MS)

8890, 5977B (from Agilent Technologies)

Injection mode: splitless

Carrier: helium

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

Column temperature: holding at 30°C for 15 minutes, then increase to 250°C at 20°C/min, and then holding at 250°C for 10 minutes. Column flow rate: 1.4 ml/min

Inlet pressure: 8.4 psi

Inlet temperature: 200°C

Injection volume: 5 μ L

Ion Source temperature: 230°C

Quadrupole temperature: 150°C

SIM (selected ion monitoring): 56 (butyl formate, 1-butanol), 117 (trimethylsilylated IPA)

[0047]

(Method for Determining Proportion of Formate Ion to IPA in Sample)

For organic acid ions and various anions contained in a sample, the organic acids were identified by a pre-concentration ion chromatography method according to the following measuring apparatus and measuring conditions, and the proportion thereof to IPA was evaluated.

[0048]

Apparatus name: ICS 2100 (from Thermo Fisher Scientific)

Anion Analysis

Detector: conductivity detector

Column: IonPac AS18

Flow rate: 1 ml/min

Temperature conditions: 30°C

Gradient conditions: 2 mM KOH → 15 minutes, 5 mM KOH → 25 minutes, 40 mM KOH → 40 minutes, 40 mM KOH

Concentration column: UTAC-LP2

Injection volume: 20 ml

Lower detection limit: 10 ppt (formate ion, acetate ion, propionate ion, butyrate ion, isobutyrate ion, fluoride ion, chloride ion, bromide ion, iodide ion, nitrate ion, nitrite ion, and sulfate ion)

[0049]

<Example 1>

A 1-inch SUS tube was attached to an autoclave (from Taiatsu Glass), SUS Heli Packs (from To-toku Engineering) were placed in the SUS tube up to a height of 50 cm, the column top was cooled with tap water so as to allow for reflux, and thus a high-pressure distillation column configured to enable a refluxed liquid to be taken out was prepared. One thousand gram of crude IPA adjusted so that the proportion of butyl formate (from FUJIFILM Wako Pure Chemical Corporation) to IPA was 10000 ppb was charged into the autoclave, and then refluxed at normal pressure for 30 minutes to discharge the gas in the system. Next, the autoclave was tightly closed, the temperature of the column bottom was set to 110°C, and the crude IPA was distilled under pressure. In this distillation, when the temperature of the column bottom reached 110°C, the absolute pressure was about 280 kPa. About 10 g of purified IPA was taken out as a distillate from the column top every 30 minutes, a total of 100 g being taken out, and the proportion

of butyl formate to IPA in the purified IPA was analyzed and found to be 90 ppb. The theoretical plate number of the high-pressure distillation column was estimated to be 12.

[0050]

<Comparative Example 1>

Crude IPA was distilled under pressure in the same manner as in Example 1 except that the autoclave was not closed and the temperature of the column bottom was set to 83°C, and purified IPA was obtained. The proportion of butyl formate to IPA in the purified IPA was analyzed and found to be 10000 ppb.

[0051]

<Example 2>

The high-pressure distillation was simulated using a process simulation software AspenPlus (from Aspen Technology, Inc.).

[0052]

Specifically, a bottom product was withdrawn from the bottom (2 L vessel) of a high-pressure distillation column having 80 trays. The high-pressure distillation column had a condenser provided at the top of the column (the uppermost tray of the column), and a part of the purified IPA condensed by the condenser was refluxed to the top of the column, while the rest of the purified IPA was taken out as a distillate.

[0053]

Crude IPA containing 10000 ppb of butyl formate as an impurity was fed at 10 L/h to a feed plate positioned 30

plates below the top of the high-pressure distillation column, and the crude IPA was subjected to high-pressure distillation. In this distillation, the temperature of the top of the column was set to 93°C, and the absolute pressure at the top of the column was set to 155 kPa. In addition, the reflux volume was set to 2.5 L/h, the reflux ratio was set to about 1.5, and the distillate was taken out from the condenser at 40 ml/h.

Further, the bottom product was withdrawn from the column bottom at about 10 mL/h so that the amount of the liquid in the column bottom 3 was maintained at about 1.5 L. The proportion of butyl formate to IPA in the purified IPA was analyzed, and found to be 10 ppb.

[0054]

<Example 3>

A simulation of the high-pressure distillation was performed in the same manner as in Example 2 except that the temperature of the top of the column was set to 101°C and the absolute pressure at the top of the column was set to 200 kPa. The proportion of butyl formate to IPA in the purified IPA was analyzed, and found to be 0.1 ppb or less.

[0055]

<Example 4>

A simulation of the high-pressure distillation was performed in the same manner as in Example 2 except that the temperature of the top of the column was set to 110°C and the absolute pressure at the top of the column was set to 275 kPa. The proportion of butyl formate to IPA in the purified IPA was

analyzed, and found to be 0.1 ppb or less.

[0056]

<Example 5>

A simulation of the high-pressure distillation was performed in the same manner as in Example 2 except that the temperature of the top of the column was set to 85°C and the absolute pressure at the top of the column was set to 110 kPa. The proportion of butyl formate to IPA in the purified IPA was analyzed, and found to be 1000 ppb.

[0057]

<Example 6>

A water-containing IPA waste liquid was collected from semiconductor manufacturing equipment including a rinsing unit for semiconductor substrates, and the three days' worth thereof was stored in the waste-liquid-receiving tank. The water-containing IPA waste liquid had a water content of 80% and an IPA content of 20%, and the proportions of impurities to IPA of 100 ppb, 21,000 ppb, 5000 ppb, and 5000 ppb for butyl formate, a formate ion, 1-butanol, and trimethylsilylated IPA, respectively. Water was fed to the waste liquid receiving tank so that the water content was 90% and the IPA content was 10% with respect to the water-containing IPA waste liquid, and a water-content-adjusted liquid was obtained as a crude isopropyl alcohol feedstock solution.

[0058]

A distillation column for low-boiling-point materials 1

shown in FIG. 2 in which the theoretical plate number was 20, a column bottom 3 was a 2-L vessel, and a condenser 2 was provided at the top of the column was used as a distillation column for low-boiling-point materials to distill the water-content-adjusted liquid 4. The water-content-adjusted liquid 4 was fed at 10 L/h to the top of the distillation column for low-boiling-point materials 1 and distilled. In this distillation, the temperature of the top of the column was set to 75 to 85°C, and the absolute pressure at the top of the column was set to 101 kPa. In addition, the reflux volume was set to 10 L/h, the reflux ratio was set to about 1000, and the distillate 5 was discharged from the condenser 2 at 10 ml/h and incinerated. Further, a first bottom product containing IPA and water was withdrawn at about 10 L/h as a bottom product 6 so that the amount of the liquid in the column bottom 3 was maintained at about 1.5 L.

[0059]

The proportion of butyl formate to IPA in the first bottom product was determined, and found to be 1 ppb or less, which was equal to or less than the lower detection limit, indicating that butyl formate was removed by the distillation column for low-boiling-point materials.

[0060]

The first bottom product was distilled using a distillation column identical to the distillation column for low-boiling-point materials 1 as a distillation column for high-boiling-point materials. Specifically, the first bottom

product was fed to a feed plate of the distillation column for high-boiling-point materials and distilled, and a first distillate containing an azeotropic mixture of IPA and water (mass ratio: 87.5:12.5) was taken out from the top of the column.

[0061]

The first distillate was fed to the feed plate of an azeotropic distillation column and subjected to azeotropic distillation. In this distillation, benzene was used as an entrainer, and benzene and water distilled from the top of the column were subjected to liquid-liquid separation; water was discarded, and the benzene was returned to the azeotropic distillation column. An IPA-containing second bottom product having a water content of 100 ppm or less was withdrawn from the column bottom.

[0062]

The proportion of butyl formate to IPA in the second bottom product was determined, and found to be 1000 ppb. This is presumed to be due to the formation of butyl formate during the removal of water in the first bottom product. The proportion of trimethylsilylated IPA to IPA in the second bottom product was determined, and found to be 2500 ppb.

[0063]

The second bottom product was distilled using, as a distillation column for low-boiling-point materials, the same distillation column as the distillation column for low-boiling-point materials 1, low-boiling-point impurities were

taken out from the top of the column, and crude IPA having the low-boiling impurities removed therefrom was obtained as a bottom product from the column bottom. The proportion of butyl formate to IPA in the crude IPA was determined, and found to be 1000 ppb. The proportion of trimethylsilyl IPA to IPA in the crude IPA was determined, and found to be less than 1 ppb, which was less than or equal to the lower detection limit.

[0064]

Crude IPA was subjected to high-pressure distillation in the same manner as in Example 1 except that the crude IPA obtained above was used, and a second distillate was taken out. The proportion of butyl formate to IPA in the second distillate was analyzed, and found to be 8 ppb.

[0065]

The second distillate was filtered through four filters of a filter having a pore diameter of 100 nm, a filter having a pore diameter of 10 nm, a cation exchange filter, and a filter having a pore diameter of 2 nm (from Entegris) to obtain purified IPA. The proportions of impurities to IPA in the purified IPA were 8 ppb, 0.5 ppb, 2 ppb, and less than 0.1 ppb for butyl formate, a formate ion, 1-butanol, and trimethylsilyl IPA, respectively.

EXPLANATION OF REFERENCE NUMERALS

[0066]

1: distillation column for low-boiling-point materials

2: condenser

3: column bottom

4: water-content-adjusted liquid

5: distillate

6: bottom product

CLAIMS

[Claim 1]

A method for producing purified isopropyl alcohol from crude isopropyl alcohol comprising butyl formate as an impurity, the method comprising:

a high-pressure distillation step of subjecting the crude isopropyl alcohol to high-pressure distillation.

[Claim 2]

The method for producing purified isopropyl alcohol according to claim 1, wherein a proportion of butyl formate to isopropyl alcohol in the crude isopropyl alcohol is 10 ppb by mass or more and 100000 ppb by mass or less.

[Claim 3]

The method for producing purified isopropyl alcohol according to claim 1 or 2, wherein the crude isopropyl alcohol is subjected to high-pressure distillation under conditions of an absolute pressure of 120 kPa or higher and 1000 kPa or lower.

[Claim 4]

The method for producing purified isopropyl alcohol according to claim 1, wherein the method further comprises a dehydration step of dehydrating a crude isopropyl alcohol feedstock solution comprising a formate ion, 1-butanol, and

water to obtain the crude isopropyl alcohol.

[Claim 5]

The method for producing purified isopropyl alcohol according to claim 4, wherein a proportion of the formate ion to isopropyl alcohol in the crude isopropyl alcohol feedstock solution is 10 ppb by mass or more and 100000 ppb by mass or less.

[Claim 6]

The method for producing purified isopropyl alcohol according to claim 4 or 5, wherein a proportion of 1-butanol to isopropyl alcohol in the crude isopropyl alcohol feedstock solution is 10 ppb by mass or more and 100000 ppb by mass or less.

[Claim 7]

The method for producing purified isopropyl alcohol according to claim 4, wherein the crude isopropyl alcohol feedstock solution is a waste liquid collected from semiconductor manufacturing equipment.