(21) International Application Number:
PCT/KR2014/006912

(22) International Filing Date:
29 July 2014 (29.07.2014)

(25) Filing Language:
English

(26) Publication Language:
English

(30) Priority Data:
10-2013-009855 120 August 2013 (20.08.2013) KR


(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

(54) Title: METHOD FOR PREPARING GLYCOL ESTER USING REACTIVE DISTILLATION

(57) Abstract: Provided is a method for preparing a glycol ester capable of increasing a conversion rate of a glycol ether under low temperature and pressure conditions, minimizing a recycled amount of unreacted materials using a reactive distillation column, and decreasing a production amount of impurities, in preparing the glycol ester using the glycol ether and a carboxylic acid. In addition, provided is a method for preparing a glycol ester for electronics capable of decreasing a loss of the glycol ester toward an upper portion of a reactive distillation column by injecting an excess amount of a carboxylic acid as compared to a molar number of a glycol ether and easily separating the glycol ester and the carboxylic acid from each other under a pressurized condition, and simplifying a subsequent separation column process without a separate azotropic distillation apparatus.
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG). Published: — with international search report (Art. 21(3))
Description

Title of Invention: METHOD FOR PREPARING GLYCOL ESTER USING REACTIVE DISTILLATION

Technical Field

1. The present invention relates to a method for continuously preparing a glycol ester from a glycol ether and a carboxylic acid using a reactive distillation column filled with a catalyst.

2. More particularly, the present invention relates to a method for continuously preparing a high purity glycol ester for electronics without including an azeotropic distillation apparatus at a subsequent step by injecting an excess amount of carboxylic acid as compared to a mole number of a glycol ether among introduced reactants.

Background Art

3. In general, glycol esters have been widely used as a solvent for a paint, an ink, an adhesive, a detergent, and the like. Various researches into a method for reacting a glycol ether with a carboxylic acid to prepare or purify a glycol ester have been conducted.

4. A method of performing an addition reaction of a glycol ether and a carboxylic acid using benzene sulfonic acid to prepare a glycol ester and performing purification using cyclohexane, which is an azeotroping solvent, has been disclosed in U.S. Patent No. 5,618,973. In the case of using this method, a product and a catalyst should be separated, and since the azeotroping solvent is used, the azeotroping solvent should be purified, such that a process becomes complicated.

5. A method of purifying a product using methyl isobutyl ketone as an azeotroping solvent has been disclosed in U.S. Patent No. 5,202,463.

6. In the case of using benzene sulfonic acid, or the like, as a catalyst as described above, the post processing is complicated, and in the case of purifying the product using the azeotroping solvent, the azeotroping solvent should be purified, it is not easy to operate a process, and losses of the glycol ether and the carboxylic acid, which are the reactants, and the glycol ester, which is the product, are generated.

7. Further, in order to produce propylene glycol mono methyl ether acetate (PMA) among the glycol esters, an esterification reaction of propylene glycol mono methyl ether (PM) and acetic acid (AA) proceeds in the presence of a homogeneous acidic catalyst. However, since the esterification reaction itself is an equilibrium reaction, there is a limitation in the level of reachable conversion through operating conditions.

8. In this case, in order to increase a reaction conversion rate, operation temperatures of a reactor and a distillation column should be increased. In addition, since there is a
high temperature corrosion property of a material in the vicinity of a boiling point (118°C) of acetic acid (AA), generally, a content of AA is decreased by injecting an excess amount of PM.

However, in the case of injecting an excess amount of propylene glycol mono methyl ether (PM), a minimum azeotrope of unconverted propylene glycol mono methyl ether (PM) and water additionally exists in addition to a minimum azeotrope of propylene glycol mono methyl ether acetate (PMA) and water, such that a distillation boundary is formed, and losses of propylene glycol mono methyl ether acetate (PMA) and propylene glycol mono methyl ether (PM) are generated toward an upper portion of the distillation column. Therefore, an azeotropic distillation technology for recovering propylene glycol mono methyl ether acetate (PMA) inside the distillation column and separating water, which is a by-product, is utilized, such that there is a problem that a process of recovering pure PMA and a process of separating the unreacted materials and water in subsequent steps are complicated.

[Disclosure of Invention]

Technical Problem

An object of the present invention is to provide a method for preparing a glycol ester for electronics capable of increasing a conversion rate of a glycol ether under low temperature and pressure conditions using a reactor and a reactive distillation column, suppressing generation of a minimum azeotrope of the glycol ether and water, and simplifying a subsequent separation process without a separate azeotropic distillation apparatus (a decanter and an azeotroping solvent injection/recovery equipment).

Another object of the present invention is to provide a method for preparing a high purity glycol ester for electronics capable of suppressing production of impurities by decreasing an injection amount of a glycol ether and separating a carboxylic acid under a pressurized condition of an atmosphere pressure or more.

Solution to Problem

In one general aspect, a method for preparing a glycol ester includes: reacting a glycol ether and a carboxylic acid with each other using a first reactor and a first distillation column; producing unreacted materials and produced water toward an upper portion of the first distillation column and producing a glycol ester containing an unreacted carboxylic acid and impurities toward a lower portion thereof; separating the unreacted materials and produced water using a second distillation column and
recycling the unreacted materials into the first reactor or the first distillation column; and separating the unreacted carboxylic acid produced toward the lower portion of the first distillation column using a third distillation column under a pressurized condition, wherein an amount of the carboxylic acid introduced in the first reactor is excess as compared to a mole number of the glycol ether, and the first distillation column is a reactive distillation column.

**Advantageous Effects of Invention**

With the method for preparing a glycol ester according to the present invention, the conversion rate of the reactant at the low operation temperature and pressure may be increased, the reflux amount may be significantly decreased, and the production amount of the impurities may be decreased even under mild reaction conditions.

In the method for preparing a glycol ester according to the present invention, the separation process at the subsequent separation process may be simplified by injecting an excess amount of carboxylic acid so that the azeotrope of the glycol ether and the produced water does not exist, and the high purity glycol ester for electronics may be provided by easily separating the carboxylic acid through the column operated under the pressurized condition.

**Brief Description of Drawings**

The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

FIG. 1 is a mimetic view of a process for preparing a glycol ester according to the present invention; and

FIG. 2 is a mimetic view of a reactive distillation column filled with a catalyst according to the present invention.

<Description of symbols of significant parts of the drawing>

1: Glycol ether feed
2: Carboxylic acid feed
3: Reactor effluent
4: Unreacted materials and water
5: Crude glycol ester and impurities
6: Unreacted carboxylic acid
7: Waste water
8: Recycled carboxylic acid
9: Glycol ester with small amounts of impurities
10: Electronic grade PMA
11: Heavies
R-100: FIRST REACTOR
V-100: FIRST DISTILLATION COLUMN
V-200: SECOND DISTILLATION COLUMN
V-300: THIRD DISTILLATION COLUMN
V-400: FOURTH DISTILLATION COLUMN

Mode for the Invention

Hereinafter, the present invention will be described in detail through exemplary embodiments and drawings, but they are provided only as illustrative examples. Meanwhile, it is obvious to those skilled in the art that the present invention is not limited to process conditions suggested in the following exemplary embodiment, but the process conditions may be optionally selected as long as an object of the present invention is achieved.

Here, technical terms and scientific terms used in the present specification have the general meaning understood by those skilled in the art to which the present invention pertains unless otherwise defined, and a description for the known function and configuration obscuring the present invention will be omitted in the following description and the accompanying drawings.

According to the present invention, there is provided a method for preparing a glycol ester includes: reacting a glycol ether and a carboxylic acid with each other using a first reactor and a first distillation column; producing unreacted materials and produced water toward an upper portion of the first distillation column and producing a glycol ester containing an unreacted carboxylic acid and impurities toward a lower portion thereof; separating the unreacted materials and produced water using a second distillation column and recycling the unreacted materials into the first reactor or the first distillation column; and separating the unreacted carboxylic acid produced toward the lower portion of the first distillation column using a third distillation column under a pressurized condition, wherein an amount of carboxylic acid introduced in the first reactor is excess as compared to a mole number of the glycol ether, and the first distillation column is a reactive distillation column.

An esterification reaction of a glycol ether and a carboxylic acid according to the present invention is an equilibrium reaction, and it is preferable for a design for increasing a conversion rate that a predetermined reactor is provided before the glycol ether and the carboxylic acid are introduced in a reactive distillation column.

The following reaction is an esterification reaction of propylene glycol mono methyl ether (PM), which is an example of the glycol ether, and acetic acid (AA), which is an example of the carboxylic acid.
The esterification reaction according to the present invention may arrive at an equilibrium state before the reactants are introduced into the first distillation column V-100.

As a non-restrictive example, the first reactor R-100 according to the present invention may be a fixed bed reactor (FBR) filled with a catalyst.

In more detail, the first reactor R-100 according to the present invention may be a fixed bed reactor (FBR) filled with a heterogeneous catalyst.

In addition, there is no need for supplement the catalyst until the catalyst reaches the end of its lifespan by using the heterogeneous catalyst, it is possible to design the reactor and the reactive distillation column at a subsequent step using a material having low corrosion resistance, and there is no need for a separate neutralization apparatus for removing a remaining catalyst.

Further, as compared to the case of using a homogenous catalyst, the above-mentioned process may be performed at a low temperature and a production amount of impurities may be minimized.

In the method for preparing a glycol ester according to the present invention, the first distillation column V-100 may include all types of reactive distillation columns capable of producing unreacted materials and produced water toward an upper portion thereof and producing a glycol ester containing an unreacted carboxylic acid and impurities toward a lower portion thereof while reacting the glycol ether and the carboxylic acid passing through the first reactor R-100 with each other.

That is, in the method for preparing a glycol ester according to the present invention, the first distillation column V-100 may be a reactive distillation column producing unreacted materials and produced water toward the upper portion thereof and producing a glycol ester containing an unreacted carboxylic acid and impurities toward the lower portion thereof.

As a non-restrictive example, the first distillation column V-100 may be a reactive distillation column including all types of packing capable of being filled in the column such as structured packing, bale type packing, and the like, as a column type filled with the catalyst, in order to simultaneously perform the reaction and separation as shown in FIG. 2.
More specifically, in the first distillation column V-100, as shown in FIG. 2, the reaction may occur in a reactive zone filled with the catalyst, and at the same time, separation of the product and the unreacted materials may proceed at a rectifying zone and a stripping zone positioned on and beneath the reactive zone.

In general, since an esterification reaction for producing a glycol ester is an equilibrium reaction as in Reaction Scheme (1), there is a limitation in a conversion rate to be obtained under reaction conditions.

However, in the first distillation column V-100 according to the present invention, as soon as the product is produced, the product is separated by the column, such that a partial pressure of the product in a reactive zone is decreased. Therefore, a production rate of the product may be increased according to Le Chatelier’s principle, such that the conversion rate may be maximized.

In this case, considering the glycol ether, which is the reactant, as a limiting reactant, the conversion rate may be defined as follows.

Total conversion rate of glycol ether (%) = [Amount of glycol ether introduced in reactor - Amount of glycol ether discharged from reactive distillation column]/ [Amount of glycol ether introduced in reactor] x 100

Equation (1)

In the method for preparing a glycol ester according to the present invention, as the conversion rate of the glycol ether is increased, an amount of the recycled glycol ether is significantly decreased, thereby making it possible to efficiently adjust a feed supply amount.

Further, as the conversion rate is increased, a loss of the glycol ether toward the upper portion of the first distillation column V-100 is decreased, such that a minimum azeotrope of the unconverted glycol ether and produced water does not exist.

Therefore, the loss of the glycol ester in the upper portion of the first distillation column V-100 may be minimized. As a non-restrictive example, a ratio of the glycol ester lost toward the upper portion to the glycol ester generated from the first distillation column V-100 may be more than 0wt% but 1.0wt% or less, preferably more than 0wt% but 0.5wt% or less.

In addition, the glycol ester containing the unreacted carboxylic acid and impurities may be produced toward the lower portion of the first distillation column V-100 according to the present invention.

Other materials except for the glycol ester, which is a desired product according to the present invention, may be contained in the impurities. As a non-restrictive example, metals may be contained in the impurities.

As a non-restrictive example, a content of the impurities contained in the glycol ester produced toward the lower portion of the first distillation column V-100 may be more
than 0wt% but 1.0wt% or less, preferably more than 0wt% but 0.5wt% or less, but is not limited thereto.

In the method for preparing a glycol ester according to the present invention, there is no need for providing a separate azeotroping solvent or azeotropic distillation apparatus, and a subsequent separation process of recovering the unconverted glycol ether and azeotroping solvent by minimizing the amount of the glycol ether in the unreacted materials produced toward the upper portion of the first distillation column V-100 to allow the minimum azeotrope of the produced water and the glycol ether not to be formed.

Further, the unreacted materials and produced water may be separated using the second distillation column V-200, and the unreacted materials separated from the second distillation column V-200 may be recycled into the first reactor R-100 or the first distillation column V-100.

Most of the unreacted materials recycled into the first reactor R-100 is the carboxylic acid, and a trace amount of the glycol ether may be contained therein.

The recycled carboxylic acid may react with the glycol ether in the first reactor R-100 and the first distillation column V-100 to prepare the glycol ester.

The unreacted carboxylic acid discharged toward the lower portion of the first distillation column V-100 according to the present invention acts as a limiting material in preparing a high purity glycol ester for electronics, and in order to separate the unreacted carboxylic acid, a separate distillation column may be provided.

That is, the unreacted carboxylic acid discharged toward the lower portion of the first distillation column V-100 according to the present invention may be separated using the third distillation column V-300 under the pressurized condition. Here, the pressurized condition means a pressure condition of an atmospheric pressure or more.

Generally, in order to separate two materials having similar boiling points, only in the case which distillation is performed under reduced pressure, a difference in relative volatility may be increased, such that separation may be easily performed. However, in the case of the glycol ester and the carboxylic acid according to the present invention, as the pressure is increased, separation may be more easily performed.

As the pressurized condition, any pressure condition may be used as long as the pressure is an atmospheric pressure or more at which the glycol ester and the carboxylic acid according to the present invention may be separated, but the pressure may be set in consideration of a high temperature pyrolysis problem of the glycol ester that may be generated as a temperature of the lower portion of the third distillation column V-300 is increased by an increase in the pressure. In distillation column, temperature is dependent on pressure and the increase of top pressure means the increase of bottom temperature.
[74] As a non-restrictive example, the pressure condition may be a pressure condition of 1 to 4.0 bar, preferably, 1.1 to 2.0 bar.

[75] The glycol ester containing the unreacted carboxylic acid and impurities may be separated by the third distillation column V-300 according to the present invention, such that the high purity glycol ester for electronics may be prepared, and a design of the present invention that the excess amount of carboxylic acid is injected into the first reactor R-100 as compared to the mole number of the glycol ether may be achieved.

[76] In the case of a general method for preparing a glycol ester performed at the condition at which an excess amount of glycol ether is injected, the glycol ether passing through a reactor and produced water form a minimum azeotrope, and thus, a distillation boundary is formed together with the minimum azeotrope of the glycol ester and the produced water, such that losses of the glycol ester and the glycol ether may be generated toward an upper portion of a distillation column.

[77] In addition, in the case of injecting an excess amount of carboxylic acid, there is a corrosion problem by the carboxylic acid depending on an operation temperature of a reactor or a distillation column, and there may be a limitation in producing a high purity product through separation of the carboxylic acid and the glycol ester at a subsequent separation process.

[78] However, in the method for preparing a glycol ester according to the present invention, formation of the distillation boundary may be suppressed by minimizing an unreacted amount of the glycol ether passing through the first reactor R-100 and the first distillation column V-100 operating at a low temperature, and the unreacted carboxylic acid discharged toward the lower portion of the first distillation column V-100 may be usefully removed by operating the third distillation column V-300 under the pressurization condition, such that an initial injection of the excess amount of carboxylic acid in preparing a high purity glycol ester for electronics may be made possible without causing a corrosive problem.

[79] That is, in the method for preparing a glycol ester according to the present invention, among the initially injected reactants, an excess amount of the carboxylic acid may be injected as compared to the mole number of the glycol ether.

[80] Here, injection of the excess amount of the carboxylic acid means that in adjusting a molar ratio of the glycol ether and the carboxylic acid corresponding to the reactants introduced into the first reactor R-100, a mole number of the carboxylic acid is higher than that of the glycol ether.

[81] As a non-restrictive example, in the method for preparing a glycol ester, an injection amount of the carboxylic acid may be 1.01 to 1.5 moles, preferably 1.1 to 1.3 moles based on 1 mole of the glycol ether.

[82] Impurities may be contained in the glycol ester passing through the third distillation
column V-300 according to the present invention, and in order to remove these impurities, a fourth distillation column V-400 may be provided.

The fourth distillation column V-400 according to the present invention may include all types of distillations columns serving to separate pure glycol ester from the impurities contained in the glycol ester.

As an example, the fourth distillation column V-400 according to the present invention may separate the pure glycol ester toward an upper portion of the column and separate heavy impurities toward a lower portion thereof.

In the method for preparing a glycol ester from a glycol ether and a carboxylic acid according to the present invention, the glycol ether includes all glycol ethers capable of achieving the object of the present invention.

A non-restrictive example of glycol ether according to the present invention may include ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, diethylene glycol mono butyl ether, or the like.

As a more specific example, in the method for preparing a glycol ester, the glycol ether may be propylene glycol monomethyl ether (PM).

In the method for preparing a glycol ester from a glycol ether and a carboxylic acid according to the present invention, the carboxylic acid may include all carboxylic acids capable of producing the glycol ester according to the present invention.

A non-restrictive example of the carboxylic acid may include propionic acid, iso-butyric acid, normal-butyreric acid, or the like. As a more specific example, in the method for preparing a glycol ester, the carboxylic acid may be acetic acid (AA), but the present invention is not limited thereto.

That is, in the case in which the glycol ether according to the present invention is propylene glycol monomethyl ether (PM) and the carboxylic acid is acetic acid (AA), the prepared glycol ester may be propylene glycol monomethyl ether acetate (PMA).

The propylene glycol monomethyl ether acetate (PMA) prepared as described above may be prepared from the first reactor and the first to fourth distillation columns and be high purity propylene glycol monomethyl ether acetate (PMA) for electronics, having a low content of acetic acid (AA).

A content of acetic acid (AA) for preparing propylene glycol monomethyl ether acetate (PMA) for electronics may be 200wtppm or less. The content can be produced 200wtppm or desirably 20wtppm or less in the present invention. In the case of the present invention, even though an excess amount of acetic acid (AA) is applied, the content of acetic acid (AA) may be lowered to 200wtppm or less, preferably, 20wtppm or less under the pressurized condition by suitably finding a column operation condition for separating propylene glycol monomethyl ether acetate (PMA) and acetic acid (AA) from each other.
Further, in propylene glycol monomethyl ether acetate (PMA) produced according to the present invention, a content of propylene glycol monomethyl ether may be 0.1 wt% or less, preferably 0.05 wt% or less, and a content of metals may be 20 ppb or less, preferably 10 ppb or less.

A reaction temperature of the first reactor R-100 according to the present invention may include all low temperature conditions at which corrosion by the carboxylic acid is not generated, but the reaction temperature may be preferably, 60 to 90°C, and more preferably, 70 to 80°C.

In the method for preparing a glycol ester according to the present invention, a temperature condition of the lower portion of the first distillation column V-100 and a pressure condition of the upper portion thereof may include all temperature and pressure conditions for preparing the glycol ester according to the present invention.

As a non-restrictive example, in the method for preparing a glycol ester, a temperature of the lower portion of the first distillation column V-100 according to the present invention may be 80 to 110°C, preferably 90 to 100°C, and a pressure of the upper portion thereof may be 0.13 to 0.27 bar, preferably, 0.13 to 0.2 bar.

Hereinafter, although Examples for describing the technical idea of the present invention in more detail will be provided, the present invention is not limited by the following Examples, but the present invention includes embodiments easily derived by a person with ordinary skill in the art.

[Example 1] Total Conversion Rate Depending on Molar ratio of PM:AA, in Case of Using First Reactor and First Distillation Column

Propylene glycol monomethyl ether (PM) and acetic acid (AA) were mixed at a molar ratio of 1:1.3 and used as raw materials. In the case of primarily reacting propylene glycol monomethyl ether (PM) and acetic acid (AA) with each other in a fixed bed reactor (FBR), 52.14% of propylene glycol monomethyl ether (PM) was converted into propylene glycol monomethyl ether acetate (PMA). At this time, the produced product was continuously injected into a first distillation column serving as a reactive distillation column filled with a catalyst at a central portion of the distillation column. In this case, the raw materials were continuously injected at operation conditions of the first distillation column at which a pressure of an upper portion of the column was maintained at 0.173319 bar, and a temperature of a lower portion of the column was maintained at 98°C. A reflux ratio in the upper portion of the column shown in FIG. 2 was maintained at 1.6. The product was analyzed using gas chromatography, and as a result, a conversion rate of propylene glycol monomethyl ether (PM) into propylene glycol monomethyl ether acetate (PMA) was 99.9% or more.

[Example 2] Total Conversion Rate Depending on Molar ratio of PM:AA, in Case of Using First Reactor and First Distillation Column
Propylene glycol monomethyl ether (PM) and acetic acid (AA) were mixed at a molar ratio of 1:1.18 and used as raw materials. In the case of primarily reacting propylene glycol monomethyl ether (PM) and acetic acid (AA) with each other in a fixed bed reactor (FBR), 49.42% of propylene glycol monomethyl ether (PM) was converted into propylene glycol monomethyl ether acetate (PMA). At this time, the produced product was continuously injected into a first distillation column serving as a reactive distillation column filled with a catalyst at a central portion of the distillation column. In this case, the raw materials were continuously injected at operation conditions of the first distillation column at which a pressure of an upper portion of the column was maintained at 0.173319bar, and a temperature of a lower portion of the column was maintained at 98°C. A reflux ratio in the upper portion of the column shown in FIG. 2 was maintained at 2.0. The product was analyzed using gas chromatography, and as a result, even though the ratio of the raw materials was decreased in the fixed bed reactor (FBR), a conversion rate of propylene glycol monomethyl ether (PM) into propylene glycol monomethyl ether acetate (PMA) was 99.9% or more.

[Comparative Example 1] Total Conversion Rate Depending on Molar ratio of PM:AA, in Case of Using only Fixed Bed Reactor

Propylene glycol monomethyl ether (PM) and acetic acid (AA) were mixed at a molar ratio of 1:1.3 and continuously injected into a fixed bed reactor (FBR) in Example 1. The product was analyzed using gas chromatography, and as a result, a conversion rate of propylene glycol monomethyl ether (PM) into propylene glycol monomethyl ether acetate (PMA) was only 52.14%.

[Comparative Example 2] Total Conversion Rate Depending on Molar ratio of PM:AA, in Case of Using only Fixed Bed Reactor

Propylene glycol monomethyl ether (PM) and acetic acid (AA) were mixed at a molar ratio of 1:1.18 and continuously injected into a fixed bed reactor (FBR) in Example 2. The product was analyzed using gas chromatography, and as a result, a conversion rate of propylene glycol monomethyl ether (PM) into propylene glycol monomethyl ether acetate (PMA) was only 49.42%.

Table 1
As shown in Table 1, the conversion rate of the glycol ether was limited by an equilibrium reaction, such that complete conversion into the glycol ester was impossible, but the total conversion rate may be increased by designing the first reactor and the first distillation column according to the present invention.

[Example 3] Rate of PMA Lost toward Upper Portion and Content of Impurities in PMA in Lower Portion, in Case of Using Excess Amount of AA

At a condition of using an excess amount of acetic acid (AA) in Example 2, compositions in upper and lower portions of the first distillation column were analyzed using gas chromatography, and as a result, as shown in Table 2, it was confirmed that a rate of propylene glycol monomethyl ether acetate (PMA) lost toward the upper portion was 0.01 wt%, a purity of propylene glycol monomethyl ether acetate (PMA) separated toward the lower portion was 98.5 wt%, and the remaining components were acetic acid (AA, 1.2 wt%) and impurities (0.3 wt%).

[Comparative Example 3] Rate of PMA Lost toward Upper Portion and Content of Impurities in PMA in Lower Portion, in Case of Using Excess Amount of PM

Propylene glycol monomethyl ether (PM) and acetic acid (AA) were mixed at a molar ratio of 1:4:1 and continuously injected into a first reactor in Example 3. The product of the first reactor was injected into a first distillation column, and in the product passing through the first reactor and the first distillation column, a total conversion rate based on acetic acid (AA) was 98% or more. In this case, the operation conditions of the first distillation column were the same as in Example 3. Compositions in upper and lower portions of the first distillation column were analyzed using gas chromatography, and as a result, as shown in Table 2, it was confirmed that a
rate of propylene glycol monomethyl ether acetate (PMA) lost toward the upper portion was 7.0wt%, a purity of propylene glycol monomethyl ether acetate (PMA) separated toward the lower portion was 96.1wt%, and the remaining components were acetic acid (AA, 1.4wt%), propylene glycol monomethyl ether (PM, 0.1wt%) and impurities (2.4wt%).

Table 2

<table>
<thead>
<tr>
<th>Operation</th>
<th>Molar Ratio of PM : AA</th>
<th>Total Conversion Rate(%)</th>
<th>Loss rate (wt%) of PMA toward Upper Portion</th>
<th>Content of Impurities (wt%) in PMA in Lower Portion</th>
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<tbody>
<tr>
<td>Example 3</td>
<td>1 : 1.18</td>
<td>99.9</td>
<td>0.01</td>
<td>0.3</td>
</tr>
<tr>
<td>Comparative</td>
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<td>98.0</td>
<td>7.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Example 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As shown in Table 2, it may be appreciated that in the case of injecting an excess amount of acetic acid (AA) introduced into the first reactor according to the present invention as compared to the mole number propylene glycol monomethyl ether (PM), the loss rate of propylene glycol monomethyl ether acetate (PMA) toward the upper portion of the first distillation column was decreased, and the content of impurities contained in the propylene glycol monomethyl ether acetate (PMA) produced toward the lower portion of the first distillation column was decreased.

Example 4 Content of AA in Glycol Ester Depending on Pressurized Condition of Third Distillation Column

A raw material in which propylene glycol monomethyl ether acetate (PMA) and acetic acid (AA) were mixed at a molar ratio of 95:5 was separated under a pressurized condition of 1.1bar. At this time, a temperature of a lower portion of the third distillation column was maintained at 150°C, and a reflux ratio in an upper portion thereof was maintained at 65.0. A composition in the lower portion of the column was analyzed using gas chromatography, and as a result, it was confirmed that a content of acetic acid (AA) in propylene glycol monomethyl ether acetate (PMA) was 20wtppm.

Example 5 Content of AA in Glycol Ester Depending on Pressurized Condition of Third Distillation Column

A raw material in which propylene glycol monomethyl ether acetate (PMA) and acetic acid (AA) were mixed at a molar ratio of 95:5 was separated under a pressurized
condition of 2.0bar. At this time, a temperature of a lower portion of the column was maintained at 172°C, and a reflux ratio in an upper portion thereof was maintained at 33.0. A composition in the lower portion of the column was analyzed using gas chromatography, and as a result, a content of acetic acid (AA) in propylene glycol monomethyl ether acetate (PMA) was not observed.

[118]  **Example 6** Content of AA in Glycol Ester Depending on Pressurized Condition of Third Distillation Column

A raw material in which propylene glycol monomethyl ether acetate (PMA) and acetic acid (AA) were mixed at a molar ratio of 95:5 was separated under a pressurized condition of 4.0bar. At this time, a temperature of a lower portion of the column was maintained at 200°C, and a reflux ratio in an upper portion thereof was maintained at 30.0. A composition in the lower portion of the column was analyzed using gas chromatography, and as a result, a content of acetic acid (AA) in propylene glycol monomethyl ether acetate (PMA) was not observed.

[120]  **Comparative Example 4** Content of AA in Glycol Ester Depending on Pressurized Condition of Third Distillation Column

A raw material in which propylene glycol monomethyl ether acetate (PMA) and acetic acid (AA) were mixed at a molar ratio of 95:5 was separated under 0.5bar. At this time, a temperature of a lower portion of the column was maintained at 128°C, and a reflux ratio in an upper portion thereof was maintained at 85.0. A composition in the lower portion of the column was analyzed using gas chromatography, and as a result, it was confirmed that a content of acetic acid (AA) in propylene glycol monomethyl ether acetate (PMA) was 95wtppm.

[122]  **Comparative Example 5** Content of AA in Glycol Ester Depending on Pressurized Condition of Third Distillation Column

A raw material in which propylene glycol monomethyl ether acetate (PMA) and acetic acid (AA) were mixed at a molar ratio of 95:5 was separated under 0.3bar. At this time, a temperature of a lower portion of the column was maintained at 116°C, and a reflux ratio in an upper portion thereof was maintained at 120.0. A composition in the lower portion of the column was analyzed using gas chromatography, and as a result, it was confirmed that a content of acetic acid (AA) in propylene glycol monomethyl ether acetate (PMA) was 323wtppm.

[124]  Table 3
As shown in Table 3, in the cases of operation at the pressure condition at which a pressure of the third distillation column according to the present invention was set to an atmospheric pressure or more, since the content of acetic acid (AA) in propylene glycol monomethyl ether acetate (PMA) corresponding to the product was low, such that PMA for electronics may be effectively prepared, and the reflux ratio of the material refluxed from the upper portion of the column through a condenser may be decreased.

It may be appreciated through the above-mentioned Examples and Comparative Examples that in the method for preparing a glycol ester according to the present invention, 99.9% or more of the glycol ether may be converted even at the small molar ratio of the raw material, such that a recycling amount was decreased by one-third or less as compared to an existing PMA preparation process not using a reactive distillation technology, such that there were advantages that an apparatus scale and utility usage may be decreased as shown in Table 4.

### Table 3

<table>
<thead>
<tr>
<th>Operation</th>
<th>Molar ratio of PMA : AA</th>
<th>Pressure Condition (bar)</th>
<th>Reflux ratio in Upper Portion of Column</th>
<th>Content of AA in PMA</th>
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<tbody>
<tr>
<td>Example 4</td>
<td>95 : 5</td>
<td>1.1</td>
<td>65.0</td>
<td>20wtppm</td>
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<tr>
<td>Example 5</td>
<td>95 : 5</td>
<td>2</td>
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<td>Example 6</td>
<td>95 : 5</td>
<td>4</td>
<td>30.0</td>
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<tr>
<td>Comparative Example 4</td>
<td>95 : 5</td>
<td>0.5</td>
<td>85.0</td>
<td>95wtppm</td>
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<tr>
<td>Comparative Example 5</td>
<td>95 : 5</td>
<td>0.3</td>
<td>120.0</td>
<td>323wtppm</td>
</tr>
</tbody>
</table>

Table 4
Further, in the case of using an excess amount of acetic acid (AA), the loss rate of propylene glycol monomethyl ether acetate (PMA) may be minimized under a more acidic atmosphere, and the content of the impurities may be decreased as compared to the existing process using an excess amount of a glycol ether. Even though the molar ratio of the excessively injected reactant is low, the total conversion rate may be increased, the content of unconverted propylene glycol monomethyl ether (PM) may be minimized, and a usage rate of expensive propylene glycol monomethyl ether (PM) may be maximized, such that economical operation conditions may be set.

In addition, the content of acetic acid (AA) in propylene glycol monomethyl ether acetate (PMA) in the lower portion of the column may sufficiently satisfy limited conditions for preparing PMA for electronics according to the present invention due to the pressurized separation conditions of the third distillation column.

**Industrial Applicability**

With the method for preparing a glycol ester according to the present invention, the conversion rate of the reactant at the low operation temperature and pressure may be increased, the reflux amount may be significantly decreased, and the production amount of the impurities may be decreased even under mild reaction conditions.

In the method for preparing a glycol ester according to the present invention, the separation process at the subsequent separation process may be simplified by injecting an excess amount of carboxylic acid so that the azeotrope of the glycol ether and the produced water does not exist, and the high purity glycol ester for electronics may be provided by easily separating the carboxylic acid through the column operated under the pressurized condition.
Claims

[Claim 1] A method for preparing a glycol ester, the method comprising:
reacting a glycol ether and a carboxylic acid with each other using a
first reactor and a first distillation column;
producing unreacted materials and produced water toward an upper
portion of the first distillation column and producing a glycol ester
containing an unreacted carboxylic acid and impurities toward a lower
portion thereof;
separating the unreacted materials and produced water using a second
distillation column and recycling the unreacted materials into the first
reactor or the first distillation column; and
separating the unreacted carboxylic acid produced toward the lower
portion of the first distillation column using a third distillation column
under a pressurized condition,
wherein an amount of the carboxylic acid introduced in the first reactor
is excess as compared to a mole number of the glycol ether, and the
first distillation column is a reactive distillation column.

[Claim 2] The method of claim 1, wherein a ratio of the glycol ester lost toward
the upper portion to the glycol ester produced from the first distillation
column is more than 0wt% but 1.0wt% or less.

[Claim 3] The method of claim 1, wherein a temperature of the lower portion of
the first distillation column is 80 to 110°C, and a pressure in the upper
portion thereof is 0.13 to 0.27bar.

[Claim 4] The method of claim 1, wherein a content of the impurities contained in
the glycol ester separated toward the lower portion of the first dis-
tillation column is more than 0wt% but 1.0wt% or less.

[Claim 5] The method of claim 1, wherein an injection amount of the carboxylic
acid is 1.01 to 1.5 moles based on 1 mole of the glycol ether.

[Claim 6] The method of claim 1, wherein the first reactor is a fixed bed reactor
(FBR) filled with a heterogeneous catalyst.

[Claim 7] The method of claim 1, wherein a reaction temperature of the first
reactor is 60 to 90°C.

[Claim 8] The method of claim 1, further comprising introducing the unreacted
carboxylic acid separated from the third distillation column into the
second distillation column.

[Claim 9] The method of claim 8, further comprising separating the impurities
contained in the glycol ester separated from the third distillation
column using a fourth distillation column.

[Claim 10] The method of any one of claims 1 to 9, wherein the glycol ether is propylene glycol monomethyl ether (PM).

[Claim 11] The method of any one of claims 1 to 9, wherein the carboxylic acid is acetic acid (AA).

[Claim 12] The method of claim 9, wherein the glycol ester separated using the fourth distillation column is propylene glycol monomethyl ether acetate (PMA).

[Claim 13] The method of claim 12, wherein a content of acetic acid (AA) contained in the propylene glycol monomethyl ether acetate (PMA) is 20wtppm or less.

[Claim 14] The method of claim 12, wherein in the propylene glycol monomethyl ether acetate (PMA), a content of propylene glycol monomethyl ether is 0.1 wt% or less, and a content of metals is 20ppb or less.

[Claim 15] The method of any one of claims 1 to 9 and claims 12 to 14, wherein a conversion rate of the glycol ether is 99% or more.
INTERNATIONAL SEARCH REPORT

PCT/KR2014/006912

A. CLASSIFICATION OF SUBJECT MATTER
C07C 67/54(2006.01)i, C07C 69/712(2006.01)i, B01J 19/24(2006.01)i

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

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C07C 67/54; C07C 67/24; C07C 67/02; C07C 69/66; C07C 69/712; B01J 19/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: glycol ester, glycol ether, carboxylic acid, reactive distillation column

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search 26 September 2014 (26.09.2014)
Date of mailing of the international search report 26 September 2014 (26.09.2014)

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## Information on Patent Family Members

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<td>TW 539668 A</td>
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<td>AU 4834297 A</td>
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<td></td>
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