

DESCRIPTION

TRIOXAN PURIFICATION PROCESS

TECHNICAL FIELD

The present invention relates to a process for purifying trioxan obtained by heating an aqueous formaldehyde solution. More particularly, it relates to a process which comprises extracting with benzene a trioxan-
5 containing distillate yielded by heating an aqueous formaldehyde solution and separating and purifying trioxan from the trioxan-containing benzene solution by continuous distillation.

10 Trioxan which the present invention envisages to provide is used as an intermediate of polymers in polyacetal resins, and in this technical field there has been an industrial call for the establishment of a process capable of producing highly purified trioxan.

15 PRIOR ART

Generally trioxan can be obtained by heating an aqueous formaldehyde solution. For industrial production of trioxan, a method has been proposed in which a 30 to 70 wt% aqueous formaldehyde solution is distilled by heating
20 in the presence of an acidic catalyst, and the resulting distillate having a composition of 20 to 55 wt% of trioxan, 10 to 35 wt% of formaldehyde, 20 to 50 wt% of water and the like is used as a crude for obtaining purified trioxan.

Water and formic acid contained in such a crude

product, the formic acid being produced as a by-product due to use of a strongly acidic catalyst for the reaction, act as a chain transfer agent to reduce the degree of polymerization when producing polyoxymethylene by polymerizing
5 trioxan, so that it has been commonly practiced to remove such substances from the produced trioxan.

Various methods, such as mentioned below, have been proposed for removing water from trioxan: adding an additive such as an isocyanate or sodium dispersion or a
10 metal hydride (JP-B-40('65)-12900, DE-A-1906846 and DE-A-1280884); adding an adsorbent such as alumina or zeolite (JP-B-44('69)-17915); carrying out distillation in the presence of a solvent which is capable of forming an azeotropic mixture with water (JP-B-49('74)-5351, GB-A-
15 1080950, JP-B-49('74)-28197 and JP-B-28('53)-518).

These methods, however, are not necessarily satisfactory for industrial applications for the reasons that after-treatments are required since side reactions occur; the process is complicated; and the effect is
20 unsatisfactory, etc.

The following methods have been proposed for removing formic acid from trioxan: rectification is carried out by adding a reagent capable of capturing formic acid, such as alkali metals, isocyanates, metal oxides and amines
25 (JP-B-40('65)-8545, JP-B-40('65)-12900, BE-647355 and JP-B-45('70)-33407); formic acid is adsorbed away by using alumina, zeolite, an ion exchange resin or the like as adsorbent (JP-B-44('69)-17915, JP-B-47('72)-7384, GB-A-

1254344, JP-B-45('70)-11503 and GB-A-1137054). A method has also been proposed which comprises heating a concentrated aqueous solution of formaldehyde in the presence of a strongly acidic catalyst to produce trioxan, extracting
5 the aqueous distillate with benzene, separating the benzene solution of trioxan to obtain crude trioxan, and purifying it by distillation (JP-B-49('74)-5351 and GB-A-1080950). These methods, however, are not favorable for industrial applications because of the necessity of using specific
10 chemicals and/or specific equipment.

As a result of extensive studies for developing an industrial process capable of producing trioxan with minimized contents of water and formic acid efficiently by a simple operation, the present inventors previously found
15 that high-quality trioxan could be obtained by extracting with benzene a solution composed of trioxan, water and formaldehyde produced from distillation of formalin by heating, and distilling the resulting benzene extract solution under the specified conditions. A patent
20 application was filed (corresponding to JP-B-64('89)-10513 and US-A-4332644) on the basis of this finding.

The process described in JP-B-64('89)-10513 and US-A-4332644 is a method for continuous distillation separation of trioxan which comprises extracting with
25 benzene a trioxan-containing distillate obtained by heating an aqueous formaldehyde solution, supplying the resultant trioxan-containing benzene solution as crude to a distillation column, distilling away benzene from the top of the

column and taking out trioxan from the bottom of the column, characterized in that the trioxan concentration X (wt%) of the liquid composition at the crude feed plate of the distillation column is kept within the range that
 5 satisfies the relation of the following formula (1):

$$100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2} \leq X \leq 100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2} + 2R^{0.5} \quad (1)$$

wherein R is a reflux ratio, and γ is a parameter defined by the following formula (2):

$$\gamma = \frac{R(1 - C/100) + q}{R(1 - C/100) - C/100 + q} \quad (2)$$

10 wherein q is a weight ratio of the liquid portion in the crude, and C is a trioxan concentration (wt%) of the crude.

According to the McCabe-Thiele theory on continuous rectification of a two-component system, the molar fraction y_{j+1} of the vapor leaving the (j+1)th plate
 15 from the top is given by the following formula (3) from the operating line in the recovery section (see, for example, Hirata and Yorimi: Distillation Engineering Handbook, page 111):

$$y_{j+1} = \frac{L + qF}{L + qF - W} X_j - \frac{W}{L + qF - W} X_w \quad (3)$$

20 wherein L is a molar flow rate of the falling liquid, F is an amount of the crude supplied, W is an amount of bottom

product, q is a ratio of the liquid portion in the crude, X_j is a molar fraction of the liquid leaving the j th plate from the top, and X_w is a molar fraction of the bottom product.

- 5 Gradient γ of the operating line in the recovery section in the above formula is given by the following formula (4):

$$\gamma = \frac{L + qF}{L + qF - W} = \frac{\frac{L}{F} + q}{\frac{L}{F} - \frac{W}{F} + q} \quad (4)$$

- and when assuming the ideal conditions for perfect separation of the low-boiling-point component and the high-boiling point component of the two-component system, the following relations hold:

$$\frac{L}{F} = R(1 - \frac{C}{100})$$

$$\frac{W}{F} = \frac{C}{100}$$

- 15 Substitution of these equals in the above formula (4) gives the following formula (5):

$$\gamma = \frac{R(1 - \frac{C}{100}) + q}{R(1 - \frac{C}{100}) - \frac{C}{100} + q} \quad (5)$$

Thus, γ can be used as a parameter indicating the ideal distillation condition. In the invention of JP-B-

64('89)-10513 and US-A-4332644 mentioned above, this γ is used as a basic parameter to specify the experimentally optimum range.

It will be understood that the formula (1) sets the liquid composition at the crude feed plate on the extension of the ideal operating line and also experimentally shows the permissible limits of the liquid composition at the feed plate of the distillation column in which it is possible to effect gas/liquid separation of benzene and trioxan and to minimize the content of the chain transfer agent in trioxan at the bottom of the distillation column.

The left-hand member of the formula (1):

$$100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2}$$

is the minimum value of trioxan concentration of the liquid composition at the feed plate of the distillation column, and the right-hand member of the formula (1):

$$100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2} + 2R^{0.5}$$

is the maximum value of the same. As is apparent from the above, the greater the reflux ratio is, the more widened are the permissible limits of the liquid composition at the crude feed plate.

In the conventional methods for distillation separation of a benzene solution of trioxan, usually the

liquid composition at the crude feed plate is made to accord with the crossing point of the operating line in the concentrated section and the crude line (q line) in the operation of the distillation column (see, for example, 5 Shigefumi Fujita and Heiichiro Tohata: Chemical Engineering III, 2n Ed., Material Transfer Operations, pp. 40-47, Tokyo Kagaku Dojin). That is, it has been the basic operation that in case the crude is in a liquid state below the boiling point, the trioxan concentration of the liquid 10 composition at the crude feed plate is made substantially equal to the crude concentration. This operation, however, makes removal of the chain transfer agent unsatisfactory.

JP-B-64('89)-10513 and US-A-4332644 discloses a potent method for providing highly purified trioxan. It 15 was found, however, that use of the method disclosed in JP-B-64('89)-10513 and US-A-4332644 is still unsatisfactory for purification of trioxan under certain specific conditions. The invention of JP-A-3('91)-123777 mentioned above provides an improvement on this point.

20 It has been difficult to obtain trioxan containing almost no water, methanol, formic acid and the like by, for example, extracting with benzene trioxan obtained by heating a methanol-rich aqueous formalin solution and separating benzene from the obtained benzene solution of 25 trioxan. Thus, the method disclosed in JP-A-3('91)-123777, in contrast to the method disclosed in JP-B-64('89)-10513 and US-A-4332644, is a trioxan purification process which can adapt itself to any possible situation by incorporating

an operation in which water is extracted with a benzene solution containing benzene-extracted trioxan. By employing this purification process, it has become possible to purify trioxan to an impurity (water, etc.) content of
5 down to about 1 ppm.

There are, however, the occasions where trioxan with an especially high degree of purification is required. In certain cases, for example, trioxan with an impurity (water, etc.) content of less than 0.5 ppm is required.
10 The present invention provides a trioxan purification process which is capable of producing trioxan with such a high degree of purification.

DISCLOSURE OF THE INVENTION

In order to find a method for purifying trioxan
15 to a higher degree than available at present under all possible conditions, the present inventors have eagerly pursued researches on the art of distillation and, as a result, surprisingly found that it is possible to purify trioxan to a higher degree by using a distillation column
20 having 30 or more plates and by setting an inflection point of the temperature profile of the distillation column at a position which is at least 10 plates away from the feed plate and at least 5 plates away from the bottom of the distillation column.

25 Thus, the present invention provides a process for purifying trioxane which comprises the steps of extracting with benzene a trioxan-containing distillate

obtained by heating an aqueous formaldehyde solution,
 supplying the resulting trioxan-containing benzene solution
 as crude to a distillation column, distilling away benzene
 from the top of the column and continuously distilling and
 5 separating trioxan from the bottom of the column, said
 distillation column having 30 or more plates, characterized
 in that:

- (i) the trioxan-containing benzene solution is
 extracted with water;
- 10 (ii) then the trioxan concentration X (wt%) of the
 liquid composition at the crude feed plate of said
 distillation column is kept within the range that satisfies
 the relation of the following formula (1):

$$100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2} \leq X \leq 100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2} + 2R^{0.5} \quad (1)$$

- 15 wherein R is a reflux ratio, and γ is a parameter defined
 by the following formula (2):

$$\gamma = \frac{R(1 - C/100) + q}{R(1 - C/100) - C/100 + q} \quad (2)$$

- wherein q is a weight ratio of the liquid portion in the
 crude, and C is a trioxan concentration (wt%) in the crude;
- 20 and

- (iii) the temperature of the distillation column is
 adjusted so that in a temperature profile of the
 distillation column where temperature is plotted as

abscissa and the number of column plates as ordinate, the inflection point of the temperature profile will appear at a position which is below the crude feed plate and at least 10 plates away therefrom and also at least 5 plates away
5 from the bottom of the column.

BEST MODE FOR CARRYING OUT THE INVENTION

In the present invention, a trioxane-containing benzene solution is extracted with water to transfer impurities such as methanol, formic acid and formaldehyde
10 present in the solution into the aqueous phase. This greatly facilitates purification of trioxan by succeeding distillation. Therefore, trioxan obtained from the distillation operation subsequently conducted after extraction is remarkably reduced in content of impurities
15 such as water, methanol and formic acid. The mechanism that derives this effect is not definitely known, but it is supposed that transfer of formaldehyde present in the trioxan-containing benzene solution into the aqueous phase by extraction with water expedites purification of trioxan
20 in the ensuing distillation operation.

Extraction with water is conducted either by a batchwise extraction system using a tank or by a continuous extraction system making use of a column. It is preferred to employ a so-called countercurrent contact system in
25 which water is passed through the column from its top while a trioxan-containing benzene solution is made to flow through the column from its bottom, and the plates or an

auxiliary substance such as filler for improving inter-
facial contact between water and the trioxan-containing
benzene solution are provided in the column. The ratio of
water to the trioxan-containing benzene solution used in
5 the present invention is in a range of 0.01 : 1 to 1 : 1,
preferably from 0.03 : 1 to 0.3 : 1, more preferably from
0.05 : 1 to 0.2 : 1. A smaller amount of water makes the
extraction effect unsatisfactory, while use of an excess
amount of water leads to poor economy because of much loss
10 of trioxan.

The formaldehyde concentration of the trioxan-
containing benzene solution after extraction with water,
though it depends on the desired degree of purification, is
usually 1% or less, preferably 0.2% or less, more
15 preferably 0.05% or less.

After extraction with water, the trioxan-
containing benzene solution is supplied into a distillation
column where benzene is separated away and trioxan with a
reduced content of impurities such as water is obtained
20 from the bottom of the column.

During the operation in the distillation column
for the above process, it is necessary to adjust the liquid
composition at the crude feed plate of the distillation
column so as to satisfy the condition expressed by the
25 formula (1). If the trioxan concentration of the liquid
composition in the crude is left below the lower limit of
the range defined by the formula (1), it becomes difficult
to effect a separation between trioxane and benzene, while

if the trioxan concentration is kept above the upper limit of the defined range, it becomes hard to lower the content of the chain transfer agent.

The trioxan concentration at the feed plate can
5 be controlled by adjusting the amount of vapor rising from the bottom of the column, changing the temperature profile in the column, or other methods. In the present invention, the temperature profile in the distillation column is particularly important.

10 In the temperature profile of the distillation column where temperature is plotted as abscissa and the number of column plates as ordinate, an inflection point of the temperature profile below the crude feed plate is set at a position which is at least 10 plates away from the
15 crude feed plate and at least 5 plates away from the bottom of the column, thereby making it possible to obtain highly purified trioxan. The position of the inflection point is at least 10 plates, preferably at least 15 plates away from the crude feed plate. The reason why the position of the
20 inflection point need be at least 10 plates away from the crude feed plate is yet to be clarified, but it is supposed that the relation between the temperature profile in the distillation column and the distillation separation behavior of trace impurities is the key factor.

25 In order that the inflection point of the temperature profile may appear at a position which is below the crude feed plate and at least 10 plates away from the crude feed plate and also at least 5 plates away from the

bottom of the column, positional adjustment is made by properly changing the supplied amount of crude to the column, reflux ratio, and feed of steam used as heating source.

5 In the distillation separation of trioxan and benzene, the reflux ratio, though it depends on the trioxan concentration in the crude solution, is usually in a range of 1.1 to 8. Although it is possible to use a higher reflux ratio than 8, an unnecessarily high reflux ratio
10 only results in causing loss of energy. The preferred reflux ratio is 1.2 to 6, more preferably 1.5 to 4.

For continuous distillation, usually a multiple-plate distillation column is used. In the present invention, the number of the plates provided in the
15 distillation column is 30 or more, but the number of the plates actually used differs depending on the desired degree of purification, crude used, reflux ratio and other factors.

The present invention will be described in more
20 detail by reference to the examples and comparative examples, but the present invention should not be restricted by these examples in any way.

Example 1

A 65% aqueous formalin solution containing 6% of
25 methanol was heated and distilled in the presence of sulfuric acid to obtain a water-soluble distillate (aqueous solution) containing 45% of trioxan, the rest consisting of

formaldehyde, methanol and water. This aqueous solution was subjected to countercurrent extraction with benzene to obtain a benzene solution containing 42% of trioxan. This trioxan-containing benzene solution was supplied into a
5 Raschig ring-packed column from the bottom thereof while water was supplied into the column from its top. The ratio of water to the trioxan-containing solution was adjusted to be 0.2 : 1 (by weight). The formaldehyde concentration in the trioxan-containing benzene solution after extraction
10 and washing with water was 0.05%, and the trioxan concentration was 38%.

This trioxan-containing benzene solution was continuously supplied to a 65-plate distillation column as a liquid at a temperature below the boiling point, with the
15 20th plate from the top selected as the crude feed plate, and rectified under the condition of a reflux ratio of 3. The distillation operation was carried out so that an inflection point of the temperature profile below the crude feed plate in the column will appear at the 15th plate from
20 the crude feed plate, thereby continuously separating benzene and trioxan, from the top of the column and the bottom of the column, respectively. As an operating condition in this process, the trioxan concentration at the feed plate was kept at 25% in conformity to the formula (1)
25 shown above.

The chain transfer agent in the obtained trioxan contained 0.1 ppm of water and 0.1 ppm of formic acid.

Comparative Example 1

The same procedure as in Example 1 was repeated except that the trioxan-containing benzene solution was not subjected to extraction and washing with water. The
5 obtained trioxan contained 90 ppm of water and 60 ppm of formic acid.

Comparative Example 2

The same procedure as in Example 1 was repeated except that as an operating condition of the distillation
10 column, the inflection point of the temperature profile below the crude feed plate in the distillation column was set at the 7th plate from the feed plate. The obtained trioxan contained 1 ppm each of water and formic acid.

Example 2

15 The same procedure as in Example 1 was repeated except that the ratio of water to the trioxan-containing benzene solution in the countercurrent extraction was changed to 0.15 : 1 (by weight). The formaldehyde concentration in the trioxan-containing benzene solution
20 after extraction and washing with water was 0.11%, and the trioxan concentration was 39%. The content of water and the content of formic acid in the trioxan after distillation purification were both 0.2 ppm.

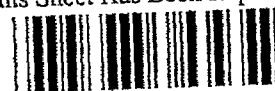
Example 3

25 The same procedure as in Example 2 was repeated except that the position of the inflection point of the temperature profile at a lower portion of the distillation column was set at the 10th plate from the crude feed plate.

The contents of water and formic acid in the obtained trioxan were both 0.3 ppm.

INDUSTRIAL APPLICABILITY

The present invention can provide highly
5 purified, high-quality trioxan of polymerization grade for
polyacetal resins, and is beneficial to the polyacetal
production industry.



CLAIMS

1. A process for purifying trioxane comprising the steps of extracting with benzene a trioxan-containing distillate obtained by heating an aqueous formaldehyde solution, supplying the resulting trioxan-containing benzene solution as crude to a distillation column, distilling away benzene from the top of the column and continuously distilling and separating trioxan from the bottom of the column, said distillation column having 30 or more plates, characterized in that:

- (i) the trioxan-containing benzene solution is extracted with water;
- (ii) then the trioxan concentration X (wt%) in the liquid composition at the crude feed plate of the distillation column is kept within the range that satisfies the relation of the following formula (1):

$$100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2} \leq X \leq 100 - \frac{50}{\gamma - 0.5} - 2(\gamma - 1)^{0.2} + 2R^{0.5} \quad (1)$$

wherein R is a reflux ratio, and γ is a parameter defined by the following formula (2):

$$\gamma = \frac{R(1 - C/100) + q}{R(1 - C/100) - C/100 + q} \quad (2)$$

wherein q is a weight ratio of the liquid portion in the crude, and C is a trioxan concentration (wt%) in the crude; and



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(iii) the temperature of the distillation column is adjusted so that in a temperature profile of the distillation column where temperature is plotted as abscissa and the number of column plates as ordinate, the inflection point of the temperature profile will appear at a position which is below the crude feed plate and at least 10 plates away from the crude feed plate and also at least 5 plates away from the bottom of the column.

2. A process according to Claim 1, wherein the temperature of the distillation column is adjusted so that in said temperature profile of the distillation column, the inflection point of the temperature profile will appear at a position which is below the crude feed plate and is at least 15 plates away from the crude feed plate and also at least 5 plates away from the bottom of the column.

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