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DESCRIPTION

PROCESS FOR PRODUCTION OF HIGH-PURITY TRIOXANE

TECHNICAL FIELD

The present invention relates to a process for producing trioxane by cyclizing formaldehyde to convert it into a cyclic trimer, and relates to a

5 process for producing high-purity trioxane by purifying efficiently the thus obtained trioxane. More particularly, the present invention relates to a process for producing high-purity trioxane comprising contacting an aqueous formaldehyde solution with an acidic catalyst

10 to prepare trioxane; extracting the thus obtained trioxane with a nonaqueous organic solvent; distilling thus obtained organic solvent solution containing trioxane in a distillation column; contacting the trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$

15 (wherein $n = 2 - 5$) (hereinafter also referred to as "oligoacetals"), taken out from the distillation column, with a solid acid catalyst in the presence of water to decompose the oligoacetals, further mixing the trioxane distillate with a nonaqueous organic solvent

20 and then washing the resulting mixture with water; and recycling the resulting trioxane-containing organic extract.

BACKGROUND ART

Generally, trioxane is synthesized by reacting aqueous formaldehyde solution in the presence of an acidic catalyst. After the reaction, the aqueous solution contains the desired trioxane, and also contains water, formaldehyde, methanol, formic acid, methylal, methyl formate, oligoacetals and other impurities, for this reason there has been proposed various methods for purification of trioxane. For example, a method for purifying trioxane by distillating a trioxane synthesis liquid, extracting the trioxane from the distillate with an organic solvent, further distillating the extract (JP-B-49-5351 and JP-A-56-87580); a method of extracting a benzene solution containing trioxane with water, then distillating the extract efficiently (JP-A-3-123777); and a method of separating and removing oligoacetals as impurities in a distillation column in which a large number of plate columns are installed and under conditions of a high reflux ratio (JP-A-57-200382). Furthermore, the present inventors disclosed an effective method for purifying trioxane by supplying an organic solution containing trioxane and further water, formaldehyde, methanol, formic acid, methylal, methyl formate and oligoacetals, to the top of a distillation column; then taking out the organic solvent, water, methanol, formic acid, methylal and methyl formate from the top of distillation column; taking out trioxane containing oligoacetals and/or an

organic solvent from the middle portion of and the bottom of the distillation column; and obtaining purified trioxane from the lower portion of the distillation column; contacting the trioxane containing
5 oligoacetals and/or the organic solvent taken out from the middle portion of and the bottom of the distillation column, with a solid acid catalyst; then returning the contacted materials to the top portion of the distillation column (JP-A-63-264579).

10 However, none of the above-mentioned known methods are good enough to remove impurities such as water, formaldehyde, methanol, formic acid, methylal and methyl formate from the objective trioxane to the utmost limit and oligoacetals efficiently.

15 In a method disclosed in the above-mentioned JP-A-63-264579, the trioxane solution containing oligoacetals is returned directly to the top portion of the distillation column after the solution is contacted with a solid acid catalyst, but the removal of formic
20 acid to the utmost limit can hardly be achieved.

DISCLOSURE OF THE INVENTION

The present inventors have made an extensive study to solve these problems of the known methods, and
25 successfully completed the present invention.

The present invention relates to a process for purifying trioxane by separating purified trioxane

in a distillation column from an organic solution containing impurities of lower boiling point (e.g. methyl formate, methylal, formaldehyde and methanol), oligoacetals and trioxane, which process comprises
5 contacting a trioxane distillate containing oligoacetals separated in the distillation column with a solid acid catalyst in the presence of water, mixing the distillate with a non-aqueous organic solvent and then washing the resulting mixture with water to obtain
10 a trioxane-containing organic extract and returning the organic extract to the distillation column.

The present invention also relates to a process for producing trioxane comprising: the step of synthesizing trioxane by heating an aqueous formal-
15 dehyde solution in the presence of an acidic catalyst to obtain a trioxane-containing aqueous solution, the step of subjecting said trioxane-containing aqueous solution to extraction with a nonaqueous organic solvent to obtain an organic solution containing
20 trioxane, $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n is 2 to 5, and at least one impurity of low boiling point, selected from the group consisting of methyl formate, methylal, formaldehyde and methanol, the step of supplying said organic solution containing trioxane to a distillation
25 column and carrying out distillation and separation to obtain a purified trioxane distillate and a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n is 2 to 5, the step of contacting a part or the whole portion

of said trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$,
wherein n is 2 to 5, with a solid acid catalyst in the
presence of water, the step of then mixing said
distillate with a non-aqueous organic solvent and then
5 washing the resulting mixture with water to obtain a
trioxane-containing organic extract, and the step of
returning said trioxane-containing organic extract to
said distillation column.

According to the present invention, an
10 extremely highly purified trioxane can be efficiently
obtained.

BEST MODE FOR CARRYING OUT THE INVENTION

Trioxane is synthesized, according to a well-
known method in the art, by heating an aqueous formal-
15 dehyde solution in the presence of an acidic catalyst.
The concentration of formaldehyde in the aqueous solu-
tion is usually 30 to 80 % by weight. As the acidic
catalyst for synthesizing trioxane, sulfuric acid,
phosphoric acid, p-toluenesulfonic acid, zeolite or a
20 cation exchanger having sulfonic acid group or fluoro-
alkylsulfonic acid group may be used generally.

Trioxane is extracted with a nonaqueous
organic solvent directly from an aqueous solution
containing the formed trioxane or from a distillate
25 obtained after concentration by distillation. As the
nonaqueous organic solvent to be used in this extrac-
tion step, there are mentioned organic solvents which

can be separated into two phases when it is mixed with water, and at the same time have a property to give less dissolving amount to the aqueous phase, and further allow trioxane to be substantially dissolved.

5 As the solvents having such properties, halogenated hydrocarbons, for example methylene chloride, chloroform, carbon tetrachloride, ethyl chloride, ethylene chloride and the like; and aromatic hydrocarbons, for example benzene, toluene, xylene and the like may be

10 mentioned.

An organic solution containing trioxane can be thus obtained, in which methyl formate, methylal, formaldehyde, methanol and oligoacetal ($\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein $n = 2 - 5$) are contained as impurities, and

15 these impurities can be separated and removed as follows. This organic solution containing trioxane may be supplied to the distillation column after washing with water.

Purification of the above-mentioned organic

20 solution containing trioxane by distillation can be carried out using one or a plural number of distillation columns.

For example, in the case of purification by distillation using one distillation column, the organic

25 solution contacting trioxane is supplied to the upper portion of the distillation column, then the organic solvent and the impurities of lower boiling point (e.g. methyl formate, methylal, formaldehyde, methanol and

formic acid) are taken out from the top of the distillation column, and one trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n is mainly 2, and/or an organic solvent are taken out from the middle portion of the column, and another trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n is mainly 3, is taken out from the bottom of the column. A purified trioxane distillate can be then taken out from the lower portion of the column.

10 In the case of purification by distillation using two distillation columns, for example, an organic solution containing trioxane as the raw material is supplied to the middle section of the first distillation column, then the impurities of lower boiling point (e.g. methyl formate, methylal, formaldehyde and methanol) and an organic solvent are taken out from the top of and the upper portion of the column and a trioxane distillate containing oilgoacetals is taken out from the bottom of the column. Then the thus
15 obtained trioxane distillate is supplied to the middle section of the second distillation column, then a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n is mainly 2, is taken out from the top of the column, and a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$,
20 wherein n is mainly 3-5, is taken out from the bottom of the column, then a purified trioxane distillate can be taken out from the lower portion of the column. In this case, distillation conditions in the first column

can be set specifically by referring to the disclosures in JP-A-3-123777. Preferable distillation conditions carried out in the second distillation column is that the reflux ratio may be 5 to 500, preferably 10 to 200, and the ratio of the amount of a trioxane distillate containing oligoacetals which is taken out from the top of the column and the ratio of the amount from the bottom of the column, to the amount of purified trioxane distillate which is taken from the lower portion of the column, may be 1/100 to 1/1, preferably 1/50 - 1/3, respectively. Oligoacetals as impurities can be removed efficiently by controlling the reflux ratio and the amounts of distillates which are taken out from the respective portions of the distillation column within the range as mentioned above.

As the distillation columns in the present invention, plate columns wherein bubble cap trays, sieve trays or the like are installed or packed columns which are filled with Raschig rings, pole rings, Dickson rings, MacMahon packings or the like for the purpose of efficiently contacting a gas phase with a liquid phase can be used.

One aspect of the present invention is to decompose $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ (wherein $n = 2 - 5$) by contacting the whole of or part of a trioxane distillate containing oligoacetals separated by distillation with a solid acid catalyst in the presence of water. The trioxane distillates containing oligoacetals taken

out from the distillation column are roughly classified into two groups, thus one trioxane distillate mainly contains $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ (wherein $n = 2$) and another trioxane distillate mainly contains $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$,
5 (wherein $n = 3 - 5$). According to the present invention, all of these trioxane distillates are mixed with each other and the resulting mixture can be contacted with a solid acid catalyst. Alternatively, a part of the trioxane distillates, for example, only a trioxane
10 distillate mainly containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$ can be contacted with a solid acid catalyst.

A trioxane distillate containing oligoacetals, in the case of containing water therein, can be contacted with a solid acid catalyst as it is.
15 However, in the case of containing no or less amount of water, an adequate amount of water is added thereto to effectively accelerate the decomposition. In such a case, the amount of water to be added is not specifically restricted, but an excess amount of water is not
20 advantageous because of a large burden to separate the excess water. Theoretical amount of water which is required for the decomposition is an equimolar quantity to $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$. Amount of water is preferably 0.005 to 50% by weight, more preferably 0.1 to 30% by weight
25 in a trioxane distillate containing oligoacetals.

As the solid acid catalyst to be used for the decomposition, an inorganic oxide complex such as acid clay, zeolite, silica-magnesia or the like; a sulfate

of a metal such as nickel, iron, cadmium or the like;
an inorganic solid acid catalyst in which silica gel,
diatomaceous earth, silicon carbide or the like is
impregnated with the above-mentioned sulfate; a cation
5 exchange resin having sulfonic acid group, fluoroalkyl-
sulfonic acid group or the like may be mentioned.
Among these solid acid catalysts, zeolite and a cation
exchange resin are preferred.

The solid acid catalyst can be used in such a
10 form that is suspended in a trioxane distillate, and
can be used effectively in the form of a fixed bed that
is packed in a cylindrical vessel equipped with a
jacket.

The amount of catalyst and the temperature of
15 decomposition may be preferably selected so that the
respective oligoacetals selectively decomposition and
the decomposition rate of trioxane is kept in a lower
level. Thus, LHSV (liquid Hourly Space Velocity) is in
a range of 0.2 to 200 hr⁻¹ and the temperature of
20 decomposition is in a range of 30 to 150°C. Preferably
LHSV is in a range of 5 to 60 hr⁻¹ and the temperature
of decomposition is in a range of 50 to 100°C.

Another aspect of the present invention is to
mix a trioxane-containing solution which also contains
25 the decomposition products of oligoacetals obtained by
contact with a solid acid catalyst, with a nonaqueous
organic solvent and then wash the resulting mixture
with water and return the thus obtained trioxane-

containing organic extract to a distillation column for recycling.

Examples of the non-aqueous organic solvent to be used in this case are the same solvents as those to be used in the organic solution containing trioxane which is firstly supplied to the distillation column, as described above. A preferable organic solvent is same as that used in the organic solution containing trioxane. This organic solvent may contain trioxane, methyl formate, methylal, formaldehyde, methanol and/or oligoacetals.

For example, preferably, an organic solution containing trioxane to be supplied to the distillation column can be per se used as a nonaqueous organic solvent so as to mix it with a trioxane-containing solution which contains the decomposition products of oligoacetals formed by a solid acid catalyst. In case the organic solution containing trioxane is supplied to the distillation column after washing with water, the organic solution containing trioxane either before or after washing with water may be used as the nonaqueous organic solvent.

The amount of the nonaqueous organic solvent used in this case is preferably determined to keep the concentration of trioxane in the organic solution in a range of 5 to 70% by weight after mixing the nonaqueous organic solvent with a trioxane-containing solution which contains decomposed products of oligoacetals.

More preferably, the nonaqueous organic solvent is used in such an amount as to keep the concentration of trioxane in a range of 20 to 60% by weight. When the concentration of trioxane is less than 5% by weight, more quantity of energy for separation between trioxane and the nonaqueous organic solvent is uneconomically required. On the other hand when the concentration of trioxane exceeds 70% by weight, it is not desirable because of a great loss of trioxane in the step of the subsequent washing with water.

After the contact with a solid acid catalyst, the trioxane-containing solution is mixed with the above-mentioned nonaqueous organic solvent and further washed with water.

For the washing with water, a batch-type extraction by use of a tank, a continuous extraction by use of a column or the like is conducted. As a preferable washing method, the so-called counter current liquid-liquid phases contacting method can be used, in which water is flown from the upper section of a column, while a mixed solution of the nonaqueous organic solvent with the trioxane-containing solution containing decomposition products of oligoacetals is flown from the lower section of the column, which is filled with column plates, packings or the like to make a good contact between the intersurfaces of water and the mixed solution. By the washing with water, the decomposition products of oligoacetals, impurities and

the like are extracted with water, and a trioxane-containing organic extract is obtained. Ratio of the amount of water to be used to the amount of the mixed solution is 1:100 to 1:1, preferably 1:30 to 1:3. When
5 water is used in only a small amount, the impurities can be extracted insufficiently, while when an excess amount of water is used it is not economical due to a great loss of trioxane, etc. Washing the extract with water is carried out at a temperature in a range of 0°C
10 to the boiling point of water or the organic solvent. Preferable the temperature is in a range of 50 to 100°C.

After the washing with water, the trioxane-containing organic extract is returned to the distillation column. The position at the distillation column
15 to which the organic extract is returned is not specifically restricted, preferably a position from the middle section to the upper section of the column is selected. Preferably, in case of using one distillation column, the extract is returned to the upper
20 section of the column, and in case of using two distillation columns, the extract is returned to the middle section of the first column.

After mixing the trioxane-containing solution
25 which contains decomposition products of oligoacetals formed by contact with a solid acid catalyst, with a nonaqueous organic solvent, when the thus obtained mixture without being treated by water-washing is

returned to the distillation column, then the resulting trioxane has a lower purity, and especially the concentration of formic acid can hardly be reduced to the utmost lower level.

5 When the trioxane distillate containing oligoacetals, which is separated from the distillation column, is discharged without being subjected to any treatment, it is economically disadvantageous due to a great loss of trioxane. On the other hand, when the
10 amount of the trioxane distillate containing oligoacetals taken out from the distillation column is kept in a small amount in order to keep the loss of trioxane as small as possible, the concentration of oligoacetals being contained in the purified trioxane distillate is
15 increased, so that highly purified trioxane cannot be obtained, or the number of column plates installed in the distillation column and the reflux ratio are necessarily be increased to very large values, as well as a large scale equipment and a large quantity of
20 energy are required for producing trioxane.

On the contrary, very highly purified trioxane can be for the first time produced continuously and efficiently by the present invention.

 The present invention will be further
25 explained in detail with reference to the following Examples. However the present invention should not be restricted thereby.

Example 1 (Present invention)

In the presence of sulfuric acid, a 60% formalin solution was heated and distilled to obtain an aqueous distillate containing trioxane from the top of a column. This aqueous distillate was mixed with benzene, and the resulting mixture was separated into two phases. Thus, a benzene solution containing 38% by weight of trioxane, 0.5% by weight of formaldehyde, 1.5% by weight of methanol, 0.5% by weight of methyl formate, 0.25% by weight of methylal, 1.5% by weight of water, 0.3% by weight of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$, and 0.05% by weight of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_3\text{CH}_3$ was obtained continuously. This benzene solution was supplied to the 20th plate section of the first distillation column (wherein 40 sieve trays were installed), and then the solution was distilled in a reflux ratio of 3. From the top of the column, benzene, formaldehyde, methanol, methyl formate, methylal, water and formic acid were taken out, and from the bottom of the column, a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ was continuously taken out. Furthermore, this trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ was supplied to the 25th plate section of the second distillation column (wherein 40 sieve trays were installed), and was distilled in a reflux ratio of 50. From the top of the second distillation column, a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$ was obtained, and from the bottom of the same column another trioxane distillate containing

$\text{CH}_3\text{O}(\text{CH}_2\text{O})_3\text{CH}_3$ was obtained, and from the 35th plate section of the second distillation column, purified trioxane distillate was taken out, continuously. The amounts of trioxane distillates being taken out from the top of and from the bottom of the distillation column were controlled respectively to keep the ratio of 1/20 by weight on the basis of the amount of the purified trioxane distillate. The trioxane distillates containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, being taken out from the top of and from the bottom of the second distillation column were combined together, and 1/10 part of water on the basis of trioxane was added thereto. The thus obtained mixture was then passed through a fixed bed which is filled with a cation exchange resin (Amberlite 200C manufactured by Organo Co., Ltd.), and the resin was kept at a temperature of 70°C , at an LHSV of 3.0 hr^{-1} . Added to 1 part by weight of the trioxane-containing solution containing decomposition products of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ was 2 parts by weight of benzene. The thus obtained benzene solution containing trioxane, was supplied to the lower portion of a packed column which is filled with Raschig rings, and water was supplied to the upper portion of the packed column. In this case, the ratio by weight of the amount of benzene solution to the amount of water was kept at 15:1, and the extraction temperature was controlled to 70°C . The benzene solution containing trioxane which was washed with water was combined with the above-mentioned

benzene solution to be supplied to the first distillation column, thereby conducting recycling. Thus, highly purified trioxane was produced continuously. The concentrations of impurities contained in the
5 purified trioxane distillates obtained from the second distillation column are shown in Table 1.

Examples 2 to 5 (Present invention)

By using an apparatus similar to that used in Example 1, the same procedures as in Example 1 were
10 carried out except that the decomposition conditions (i.e. the amounts of water added and the values of LHSV) of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ in the trioxane distillates containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ which were taken out from the top of and from the bottom of the second distillation
15 column, the ratios of mixing trioxane solution with benzene, and the conditions of washing with water, were changed as shown in Table 1. The concentrations of impurities contained in the purified trioxane distillate obtained from the second distillation column are
20 shown in Table 1.

Example 6 (Present invention)

In the presence of sulfuric acid, a 65% formalin solution was heated and distilled to obtain an aqueous distillate from the top of a column. This
25 aqueous distillate was mixed with benzene, and the resulting mixture was separated into two phases. Thus,

a benzene solution containing 38% by weight of trioxane, 2.5% by weight of formaldehyde, 1.5% by weight of methanol, 0.5% by weight of methyl formate, 0.25% by weight of methylal, 1.5% by weight of water, 0.3% by weight of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$ and 0.05% by weight of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_3\text{CH}_3$ was obtained continuously. This benzene solution was supplied to the lower portion of a packed column which is filled with Raschig rings, and water was supplied from upper portion of the column. Ratio by weight of the amount of benzene solution to the amount of water was kept to 15:1, and the extraction temperature was controlled to 70°C. The thus extracted benzene solution containing trioxane was supplied to the 20th plate section of the first distillation column (wherein 40 sieve trays were installed) and then distilled in a reflux ratio of 3. From the top of the distillation column, benzene, formaldehyde, methanol, methyl formate, methylal, water and formic acid were taken out; and from the bottom of the distillation column, a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ was continuously taken out. Furthermore, this trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ was supplied to the 25th plate section of the second distillation column (wherein 40 sieve trays were installed) and then distilled in a reflux ratio of 50. From the top of the distillation column, a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$, and from the bottom of the distillation column, a trioxane distil-

late containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_3\text{CH}_3$ and from the 35th plate section of the distillation column, a purified trioxane distillate were taken out continuously. In this case, the amounts of trioxane distillates being taken out

5 from the top of and from the bottom of the distillation column were each controlled to be 1/10 part by weight on the basis of the purified trioxane distillate. The trioxane distillates taken out from the top of and from the bottom of the second distillation column, contain-

10 ing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, were combined together, and water was added thereto in an amount of 1/10 part on the basis of trioxane, and this mixture was then passed in a fixed bed which is filled with a cation exchange resin (Amberlite 200C, manufactured by Organo Co.,

15 Ltd.) kept at a temperature of 70°C at an LHSV of 3.0 hr^{-1} . The obtained trioxane-containing solution which contains decomposition products of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ was combined into the stream of the benzene solution to be supplied to the first distillation column, and the both

20 solutions were washed with water at the same time, then these solutions were returned to the distillation column to conduct recycling. Thus, highly purified trioxane was produced continuously. The concentrations of impurities contained in the purified trioxane

25 distillate obtained from the second distillation column are shown in Table 1.

Examples 7 and 8 (Comparison)

By using an apparatus similar to that used in Example 1, the trioxane distillates which were taken out from the top of and from the bottom of the second distillation column, and contains $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, were combined together, and water was added thereto in an amount of 1/10 part on the basis of trioxane, then this mixture was passed through in fixed bed which is filled with a cation exchange resin (Amberlite 200C, manufactured by Organo Co., Ltd.) which was kept at a temperature of 70°C , at an LHSV of 3.0 hr^{-1} . The thus obtained passed solution was combined into the stream of the benzene solution to be supplied to the first distillation column and then recycled. Except for this operation, the same procedures were conducted as in Example 1 under conditions as shown in Table 1. The concentrations of impurities contained in the high-purity trioxane distillate obtained are shown in Table 1. In comparison with the examples according to the present invention, the concentrations of water and formic acid were increased.

Table 1

Example No.	Conditions of decomposition of $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$		Concentration of trioxane after mixing of trioxane- containing solution with benzene [% by weight]	Amount of water to benzene solution in washing with water [Ratio by weight]
	Added amount of water [Ratio by weight] (To trioxane)	LHSV [hr ⁻¹]		
Example 1	1/10	3.0	33	1/10
Example 2	1/10	3.0	50	1/15
Example 3	1/10	3.0	33	1/30
Example 4	1/30	3.0	33	1/20
Example 5	1/30	10.0	33	1/20
Example 6	1/10	3.0	38	1/20
Example 7	1/10	3.0	-	-
Example 8	1/10	3.0	-	-

- to be continued -

Table 1 (cont'd)

Concentration of impurities contained in purified trioxane distillate [ppm]			
Water	Formic acid	$\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$	$\text{CH}_3\text{O}(\text{CH}_2\text{O})_3\text{CH}_3$
< 1	1	43	32
< 1	< 1	61	55
< 1	< 1	52	38
< 1	< 1	63	62
< 1	1	66	65
< 1	< 1	45	38
5	8	45	38
3	5	66	68

CLAIMS



1. A process for purifying trioxane comprising;
(i) the step of supplying an organic solution contain-
ing trioxane, $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n is 2 to 5, and
5 at least one impurity of low boiling point, selected
from the group consisting of methyl formate, methylal,
formaldehyde and methanol (hereinafter simply also
referred to as organic solution containing trioxane) to
a distillation column and carrying out distillation and
10 separation to obtain a purified trioxane distillate and
a trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein
 n is 2 to 5, (ii) the step of contacting a part or the
whole portion of said distillate with a solid acid
catalyst in the presence of water, (iii) the step of
15 then mixing said distillate with a nonaqueous organic
solvent and then washing the resulting mixture with
water to obtain a trioxane-containing organic extract,
and (iv) the step of returning said trioxane-containing
organic extract to said distillation column.

20 2. A process according to Claim 1, wherein said
organic solution containing trioxane in the step (i) is
used as said nonaqueous organic solvent.

3. A process for producing trioxane comprising:
(i) the step of synthesizing trioxane by heating an
25 aqueous formaldehyde solution in the presence of an
acidic catalyst to obtain a trioxane-containing aqueous
solution, (ii) the step of subjecting said trioxane-



containing aqueous solution to extraction with a
nonaqueous organic solvent to obtain an organic
solution containing trioxane, $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n
is 2 to 5, and at least one impurity of low boiling
5 point, selected from the group consisting of methyl
formate, methylal, formaldehyde and methanol, (iii) the
step of supplying said organic solution containing
trioxane to a distillation column and carrying out
distillation and separation to obtain a purified
10 trioxane distillate and a trioxane distillate contain-
ing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n is 2 to 5, (iv) the step
of contacting a part or the whole portion of said
trioxane distillate containing $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$, wherein n
is 2 to 5, with a solid acid catalyst in the presence
15 of water, (v) the step of then mixing said distillate
with a non-aqueous organic solvent and then washing the
resulting mixture with water to obtain a trioxane-
containing organic extract, and (vi) the step of
returning said trioxane-containing organic extract to
20 said distillation column.

4. A process according to Claim 3, wherein said
organic solution containing trioxane in the step (iii)
is used as said nonaqueous organic solvent in the step
(v).