



(86) Date de dépôt PCT/PCT Filing Date: 1997/01/21
(87) Date publication PCT/PCT Publication Date: 1997/07/31
(45) Date de délivrance/Issue Date: 2006/05/16
(85) Entrée phase nationale/National Entry: 1998/07/13
(86) N° demande PCT/PCT Application No.: EP 1997/000271
(87) N° publication PCT/PCT Publication No.: 1997/027164
(30) Priorité/Priority: 1996/01/22 (DE196 02 116.2)

(51) Cl.Int./Int.Cl. *C07C 29/94* (2006.01),
C08G 63/12 (2006.01), *C07C 31/20* (2006.01),
C07C 29/80 (2006.01)
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(54) Titre : PROCÉDE D'OBTENTION DE GLYCOLS A FAIBLE TENEUR EN ALDEHYDE
(54) Title: METHOD OF OBTAINING GLYCOLS HAVING A LOW ALDEHYDE CONTENT

(57) Abrégé/Abstract:

The invention relates to a process for obtaining glycols of low aldehyde content in which the plant used to obtain the glycol(s) is surface-treated, in whole or in part, with at least one reductive phosphorus compound.

ABSTRACT

The invention relates to a process for obtaining glycols of low aldehyde content in which the plant used to obtain the glycol(s) is surface-treated, in whole or in part, with at least one reductive phosphorus compound.

Method Of Obtaining Glycols Having a Low Aldehyde Content

5 The present invention relates to a process for obtaining glycols of low aldehyde content and to products prepared using these glycols.

10 Glycols of low molecular mass, such as mono-, di- and triethylene glycol, are important products of the chemical industry. Monoethylene glycol in particular (also referred to as 1,2-ethanediol, ethylene glycol or simply MEG) is among the principal products of the chemical industry worldwide, and is used predominantly as antifreeze for vehicle radiators and as raw
15 material for the production of polyesters.

The only process currently used for the large-scale industrial production of ethylene glycol comprises the hydrolysis of ethylene oxide and the subsequent working up of the resulting
20 reaction mixture. Worldwide production capacity for ethylene glycol produced by ethylene oxide hydrolysis is currently estimated at 7×10^6 metric tonnes per annum. In this preparation process, the ethylene oxide is reacted continuously or in batches with water, in special reactors and under appropriate conditions.
25 The resulting aqueous reaction mixture is then concentrated over several stages, and the crude glycol, finally, is purified by fractionation (cf. eg.: K. Weissermel, H.-J. Arpe, Industrielle Organische Chemie [Industrial Organic Chemistry], 3rd ed., VCH 1988, p. 159 ff.). The principal components of the reaction
30 mixture are typically mono-, di- and triethylene glycol. Tetraethylene glycol and higher homologs are usually present in quantities so small that they are generally not worth recovering.

35 Distillation processes and apparatus for the purification of glycols, of various design, are known (cf. eg.: Ullmanns Encyklopädie der technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], 4th edition, VCH 1974, Volume 8, p. 200 ff.). In the majority of cases, in serial distillation columns, first water and then ethylene glycol and, finally, the higher
40 glycol ethers are recovered continuously. Various units can be used as evaporators for the distillations; modern continuous plants, however, employ falling-film evaporators for energy reasons. For reasons of cost, these plant components are commonly
45 made from carbon steel.

Owing to the high boiling points of ethylene glycol and its homologs, the distillations always take place under reduced pressure. Any vacuum distillation unit, whether industrial-scale or laboratory-scale, possesses a certain leakage rate, ie. leaks
5 which to a minor extent allow the surrounding atmosphere to enter the unit. Thus, in the course of operation, atmospheric oxygen finds its way into the vacuum distillation.

Like all alcohols, glycols can readily be oxidized both thermally
10 (autoxidation) and catalytically. The reaction products of ethylene glycol with oxygen or other oxidizing agents are aldehydes (glycol aldehyde, glyoxal, formaldehyde, acetaldehyde) and the corresponding acids. On the other hand, however,
15 especially when ethylene glycol is used to produce polyester films, there are particularly high purity requirements. Films produced using aldehyde-rich ethylene glycol prove to be highly sensitive to light. In particular, slight yellowing can be observed. Therefore, in the course of polyester production but
20 also in other sectors, the presence of these oxidation products is extremely undesirable, so that the users are attempting to limit the aldehyde content by means of strict specification. For example, the aldehyde content of ethylene glycol intended for film production should be less than 20 ppm.

25 Provided no particular effects occur in the course of ethylene glycol production, the quantity of oxidation products formed is normally unimportant. However, it has been observed in industrial plants that a rise in the proportion of aldehyde in the distilled
30 glycol may occur which was not readily explainable. At the same time, unusually large quantities of rust particles (magnetite) were found in the liquid phases of the distillation.

The problem set out above of increased aldehyde formation should
35 also exist in the context of the distillative purification of ethylene glycol which has been prepared by other synthesis routes, for example the catalytic oxidation of ethylene in acetic acid.

40 Moreover, it is known that in large-scale industrial processes such as, for example, the manufacture of polyester fiber, large quantities of liquid, glycol-containing residues are produced. Recovery of the glycols present in these residues is reasonable from an economic standpoint. Finally, large quantities of
45 ethylene glycol are produced in the form of used radiator fluid or used antifreeze, from which the glycol can likewise be recovered. In the distillative working up of these wastes,

however, there is likewise the problem of unwanted aldehyde formation. A further factor is that the wastes may already contain small quantities of aldehyde, presenting an additional hindrance to the preparation of pure, i.e. essentially
5 aldehyde-free, glycols.

The term "glycol" as used herein embraces monoethylene glycol in particular and also the distillable homologs thereof, such as di-, tri- and tetraethylene glycol.
10

It is an object of the present invention, therefore, to provide a process which makes it possible to obtain glycols whose aldehyde content is markedly reduced. A particular object is to provide monoethylene glycol which reliably conforms to the strict
15 specifications applying to starting materials for the production of polyester.

Surprisingly, we have found that this object is achieved by providing a process for obtaining glycols of low aldehyde content
20 from glycol-containing mixtures, in which the plant used for the recovery of glycol is surface-treated, in whole or in part, with at least one reductive phosphorus compound. The intention is to treat at least those parts of the plant which come into contact
25 with a glycol in the course of working up the mixture.

The surface treatment is intended in particular to be carried out on the inner faces of those parts of the plant which are permanently or temporarily in contact with a glycol in vapor form
30 during the working up of the mixture. This applies in particular to plant components where processes are carried out at elevated temperature and to those produced from corrodable material, for example steel. This may be the case, for example, with
evaporators and their feed and discharge pipes, distillation
35 columns and reactors. In all of these plant components it is possible for vapor spaces to form in which the unwanted formation of aldehyde can take place at the temperatures prevailing therein.

40 In accordance with the invention this surface treatment can be carried out discontinuously or continuously. In the case of a discontinuous procedure, the plant components required for separating the mixture can be treated, in whole or in part, with the phosphorus compound before the mixture is processed, for
45 example, the distillation column used for the vacuum distillation of monoethylene glycol can be treated with the phosphorus compound if monoethylene glycol low in aldehyde is to be

produced. For the discontinuous procedure, the surface treatment can be carried out, for example, before processing each batch of mixture to be worked up, or else at other appropriate intervals of time. This is dependent on the severity of the reformation of aldehyde which is observed in the case of separation.

If, on the other hand, operation is continuous, then the phosphorus compound can be added to the glycol-containing mixture prior to separation. The phosphorus-containing mixture can then be separated in the plant. In accordance with the invention it is particularly preferred to meter the phosphorus compound into the mixture continuously, directly before separation. This is particularly advisable if it is expected that the mixture to be separated contains aldehyde even before separation. By this means it is possible to reduce these aldehydes by means of the phosphorus compound even before the actual separation step. If it is desired, for example, to prepare monoethylene glycol low in aldehyde, then the phosphorus compound can be added continuously, directly before introduction into the vacuum distillation column which is used for monoethylene glycol separation, to a glycol-containing mixture produced, for example, by continuous hydrolysis of ethylene oxide.

A combination of continuous and discontinuous procedure is likewise conceivable.

The phosphorus compound used in accordance with the invention may be any organic or inorganic phosphorus compound or a combination of organic and inorganic phosphorus compounds showing the desired reductive effect. The phosphorus compound applied comprises a reductive P^{+3} -containing species. Preferably it is chosen from phosphorous acid (which is predominantly in the stable tautomeric form $HP(O)(OH)_2$, which is also called phosphonic acid; cf. Römpp Chemie Lexikon [Römpp's Chemical Dictionary], 9th ed.) and the salts thereof. Salts of phosphorous acid are preferably selected from water-soluble salts such as, in particular, alkali metal phosphites, zinc phosphites and calcium phosphites. Particularly preferred alkali metal phosphites are sodium phosphite and potassium phosphite. The corresponding hydrogen phosphites can also be used. What is most preferred, however, is to use the acid itself.

If the phosphorus compound is added to the mixture itself, this addition is usually made such that the phosphorus compound is present in a proportion of from about 10 to about 5000 ppm before glycol is removed from the mixture. The proportion should

preferably be in the range from about 100 to about 1000 ppm, and should in particular be about 500 ppm. The phosphorus compound is preferably added as a solution in a glycol, such as monoethylene glycol.

5

If the plant is to be surface-treated discontinuously with the phosphorus compound, then a solution is prepared containing the phosphorus compound in a proportion of about 0.1 to 10% by weight, preferably from about 0.5 to 5% by weight, based on the overall weight of the solution. The phosphorus compound can be dissolved in a suitable organic solvent, for example monoethylene glycol, or in an aqueous solvent, for example water. An aqueous solution is preferably used. The solution prepared in this way is then used to treat those parts of the plant which are required for separating the mixture. Treatment can be carried out, for example, by flooding the relevant parts of the plant with the solution and incubating them for a suitable period. An alternative possibility would be flushing of the parts of the plant, allowing the solution to circulate for an appropriate period by pumping it around the plant parts. Also conceivable is spraying or irrigation of the parts of the plant. The necessary treatment period can be determined by the skilled worker without great difficulty, and may, for example, be from about 2 to 8 hours, for instance 4 to 6 hours. Treatment can be carried out at ambient temperatures or, for example, with heated aqueous solution (heated for example at 40-80°C).

Working up of the glycol-containing mixture in accordance with the invention produces, in particular, ethylene glycol of surprisingly low aldehyde content, the latter being in the region of less than about 20 ppm, for example about 10-20 ppm. Surprisingly, the novel process makes it possible to conform reliably to the strict specifications for ethylene glycol as apply, in particular, to the production of polyester fibers and films.

Without being limited to the following explanation, the surprising effect observed in accordance with the invention can be explained as follows:

The autoxidation of ethylene glycol, ie. the direct reaction with oxygen without a catalyst, is a slow process. In laboratory experiments where glycol is subjected, under the conditions of a typical vacuum distillation, to the oxygen which penetrates as a result of the natural leakage rate, only a slow and small increase in the aldehyde levels is observed. This is particularly

the case when these experiments are carried out in apparatus made of inert materials (e.g. glass). Even artificial leakage rates involving increased supply of oxygen lead to no drastic worsening of these levels.

5

If, however, iron bodies (eg. filings) are introduced into the same experimental setup in such a way that they are able to come into contact with the vapor phase over the distilled glycol, then, at an identical leakage rate, aldehyde contents increased
10 by a multiple are observed. At the same time, corrosion occurs to a certain extent on the iron surfaces, forming primarily magnetite (rust).

15 Even with pure magnetite instead of iron filings, the same increased formation of aldehyde is observed. However, if iron filings or magnetite are in liquid (for example in the liquid distillation phase), so that no gas-phase contact is possible, then the increased formation of aldehyde is also absent.

20

The formation of magnetite as a protective coating in plant components made of iron is known per se and is indeed desirable. Under certain circumstances, however, particles may be detached from a compact magnetite coating and, having passed to another
25 part of the plant, catalytically promote the oxidation of glycol. Indeed, such magnetite particles may occasionally be isolated by filtration in small quantities in the course of processes which are in operation. If these particles arise continuously; then the plant must be protected against corrosion by another means.

30

By the novel addition of phosphorous acid and/or phosphites to the feed streams of the distillations it is possible to prevent both corrosion, with formation of magnetite, and the unwanted oxidation of glycol.

35

The present invention is now illustrated in more detail with reference to the following working examples.

40 Working examples

Using the experiments described in Examples 1 to 4, the effect of the plant material on the formation of aldehyde from ethylene glycol was investigated:

45

Example 1

Distillation experiments with ethylene glycol

Ethylene glycol (700-800 ml) was first of all distilled at 200 mbar and a liquid-phase temperature of 150-160°C in a simple
 5 distillation apparatus consisting of distillation boiler with boiling capillary, packed column (l = 40 cm; d = 2.5 cm), descending condenser, receiver and device for producing reduced pressure. 13% liquid phase was allowed; the duration of the
 10 experiment was about 2 h. Glass rings or iron rings were used as packing for the column. Either air or nitrogen was bubbled in via the boiling capillary.

The results are compiled in Table 1 below:

15

Table 1:

Distillation of glycol over glass or iron packing

Conditions:		Packing			
		Glass		Iron	
		Aldehyde (ppm) 1) 3)			
		free	total ²⁾	free	total ²⁾
25 Air	Distil- late	27	38	42	53
	Liquid phase	<5	51	30	55
	Balance	24	40	40	53
35 Nitrogen	Distil- late	14	25	24	30
	Liquid phase	<5	57	12	52
	Balance	13	29	22	33

40

1) Initial aldehyde levels: free = 15 ppm; total = 22 ppm

2) The difference between free aldehyde and total aldehyde is the so-called bound aldehyde which in the present case, especially in the form of the acetals, escapes direct determina-
 45 tion.

- 3) The aldehyde levels were determined in accordance with the MBTH method, a photometric method for free and bound aldehyde (similar to E. Savicky et al., *Analyt.Chem.*, 33, (1961), 93-96).

5

The overall aldehyde contents which are balanced (ie. obtained taking into account the liquid phase: distillate ratio of 13:87) from the table are particularly important for interpreting the analytical data.

10

In the presence of air, an increase in the total aldehyde content is observed which, however, is much greater in the case of the iron packing. Moreover, on this packing a granular, readily movable black magnetite coating is formed.

15

If the distillation is carried out under nitrogen, the formation of aldehyde is substantially smaller to virtually negligible.

20 Example 2

Reflux experiments

25 In further experiments, glycol was heated under reflux, ie. without distillative removal, in the apparatus according to Example 1 and under otherwise largely identical conditions. In this way, contact between vapor space and the material being investigated can be maintained over a longer period, so that the
30 posited effects are able to occur to a greater extent.

The column was operated either as a pure glass column (empty) or filled with iron filings. The latter experimental setup simulates a reflux condenser of iron or a corresponding evaporator with
35 gas-phase contact.

The results are compiled in Table 2.

Table 2:

40 Refluxing of glycol in the presence of iron packing in the gas phase

45

Experiment No.	Time (h)	Atmosphere	Aldehyde ^{1) 3)} [ppm]
1	13	Air	162
2	14	Air	180
3	12	Nitrogen	40
4 ²⁾	20	Air	38

- 1) Total aldehyde
 2) Control experiment in glass
 3) Initial aldehyde level 23 ppm

It is observed that, with the ingress of air at the iron surface, ethylene glycol forms a large quantity of aldehyde in a relatively short time.

Comparison in particular with the blank experiment (No. 4), which despite a prolonged running time (20 hours) shows an increase in the aldehyde content by only 15 ppm, makes clear the connection between aldehyde formation and iron surface. In the course of the experiments in the presence of oxygen, the iron surface becomes covered with a dark oxide layer.

Example 3

Refluxing in the immersed phase

Pure monoethylene glycol (MEG) was refluxed in a glass apparatus according to Example 1 ($p = 200$ mbar; $T = 150-160^{\circ}\text{C}$). Iron filings were placed in the liquid phase, entirely immersed, and were therefore unable to come into contact with the gas phase. Air was again bubbled in via the boiling capillary. Table 3 shows the measured total aldehyde levels at the end of the experiments.

Table 3:

Refluxing of glycol in the presence of iron packings in immersed phase

No.	Material	Atmosphere	Aldehyde ¹⁾ [ppm]
5 1	Glass	Air	38
2	Glass + iron (immersed)	Air	39
10			1) Initial levels 23 ppm

Accordingly, iron in immersed phase shows the same behavior as the empty glass apparatus; the increased formation of aldehyde in the previous experiments must therefore take place in the gas phase.

Example 4

20 Pretreatment with phosphorous acid

In two parallel experiments, a glass column was filled with the following packings:

- (1) untreated filings
25 (2) filings which had been stored overnight beforehand in a 1% strength solution of phosphorous acid in glycol.

The experimental procedure was as in Example 2.

30 The results are compiled in Table 4.

Table 4:
Effect of pretreating the packing with phosphorous acid

No.	Treatment	Duration [h]	Total aldehyde [ppm] ¹⁾
1	/	12	162
40 2	H ₃ PO ₃	45	40

1) Initial levels 23 ppm

45 With the ingress of air, aldehyde is produced in the case of the untreated iron filings, with the simultaneous formation and deposition of magnetite.

In the case of the treated iron filings, this corrosion occurs virtually not at all and the liquid phase remains almost clear.

The proportion of re-formed aldehyde is substantially lower than
5 in the first case.

In the case of treatment with phosphorous acid, the filings become coated with a green covering which is retained over the
10 duration of the experiment.

Example 5

Operational experiment

15

An operational experiment was carried out in a continuous production plant which operates essentially in accordance with the scheme shown in attached Fig. 1. After H₂O and ethylene oxide (EO) have been reacted in the reactor (1) and the crude product
20 has been dewatered in the drying column (2), phosphorous acid (dissolved in monoethylene glycol) at a concentration of 20 ppm is metered in continuously to the ethylene glycol mixture after it has passed through the evaporator (3) and before it enters the
25 distillation column (4). A marked reduction in the total aldehyde content in the pure monoethylene glycol (MEG) is observed (cf. Table 5).

Table 5:

30 Reduction in the total aldehyde content in monoethylene glycol prepared on the industrial scale

Aldehyde in the Reaction mixture	Aldehyde in MEG fraction	Equilibrium after
10 - 30 ppm	< 10 ppm	2 hours

40 At the same time, there is also a reduction in the amount of rust or magnetite which can be removed by filtration from the liquid-phase discharge of the distillation.

If desired, H₃PO₃ can also be metered in directly before the
45 distillation columns (5) and (6), should the preparation of diethylene glycol (DEG) or triethylene glycol (TEG) of low aldehyde content be required.

Claims:

1. A process for obtaining glycols with low aldehyde content from glycol-containing mixtures, which comprises surface-treating the plant components produced from corrodible material, used for glycol recovery, in whole or in part, with at least one reductive phosphorous compound wherein the phosphorous compound is added to the glycol-containing mixture before or during the working up of the mixture; and subsequently the glycol(s) is (are) removed from the reaction mixture by distillation and wherein, optionally, the plant components used for the working up of the mixture are, in whole or in part, pre-treated with the reductive phosphorous compound.

2. A process as claimed in claim 1, wherein surface treatment discontinuously takes place at least in those areas of the plant which, permanently or temporarily, are in contact with glycol in vapor form in the course of working up.

3. A process as claimed in claim 1, wherein the phosphorous compound is metered continuously into the glycol-containing mixture in a proportion of from about 10 to about 5000 ppm, mixing is carried out if desired and then the glycol(s) is (are) separated off from the mixture.

4. A process as claimed in claim 1 or 2, wherein the plant is discontinuously pretreated, in whole or in part, with a solution which contains the phosphorous compound in a proportion of from 0.1 to about 10% by weight.

5. A process as claimed in claim 4, wherein the plant, in whole or in part, is flushed, flooded, irrigated or sprayed with the solution.

6. A process as claimed in any one of claims 1 to 5, wherein the phosphorous compound is selected from phosphorous acid and the salts thereof.

7. A process as claimed in claim 6, wherein the salt of phosphorous acid is a water-soluble salt.

8. A process as claimed in claim 7, wherein the water-soluble salt is selected from the group consisting of metal phosphites, calcium phosphites and zinc phosphites.

9. A process as claimed in any one of claims 1 to 8, wherein the glycol-containing mixture to be processed is a reaction mixture from the production of ethylene glycol.

10. A process as claimed in any one of claims 1 to 8, wherein the glycol-containing mixture to be processed is liquid waste.

11. A process as claimed in claim 10, wherein the liquid waste is selected from the group consisting of used radiator fluid, used antifreeze liquids, and liquid waste from residues from chemical production.

12. A process as claimed in any one of claims 1 to 11, wherein one or more of monoethylene glycol, diethylene glycol and triethylene glycol, each of low aldehyde content, are obtained.

Fig. 1

