

PROCESS FOR THE REMOVAL OF ALDEHYDES AND ACETALS
FROM INDUSTRIALLY PREPARED ACETIC ACID

The present invention relates to a process for the removal of aldehydes and acetals from industrially prepared acetic acid as arises, in particular, in the catalytic oxidation of acetaldehyde and the carbonylation
5 of methanol.

Industrially prepared acetic acid, depending on the production process, contains impurities such as formic acid, acetates, formates, acetaldehyde and formaldehyde. To achieve higher specification grades such as, for
10 example, the quality "chemically pure", the content of these impurities in the acetic acid must be reduced as far as possible. An analytical measure for this is the chromic acid test by the analytical method specified in the Deutsches Arzneibuch [German Pharmacopoeia] 10
15 (1991), by which the content of oxidizable impurities can be quantitatively determined in the acetic acid.

In addition to the said compounds which can be separated off by distillation, there are also impurities which boil in the range of the boiling point of acetic acid and can
20 therefore not be removed by distillation. These are principally the addition or condensation products of aldehydes, in particular oxidizable hemiacetals and complete acetals such as, for example, formaldehyde methyl acetyl acetal (methoxymethyl acetate;
25 b.p. 117-118°C) or acetaldehyde diacetyl acetal (1,1-diacetoxyethane; b.p. 169°C). Since these compounds are also determined by the chromic acid test, only

unsatisfactory yields of chemically pure acetic acid in conformance with specifications are obtainable by means of a distillation.

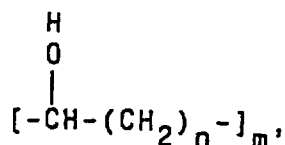
For the removal of the aldehydes and acetals, therefore,
5 potassium dichromate has been proposed in US-A-4 061 546 and potassium permanganate has been proposed in DE-A-21 04 828 as oxidants. Pure acetic acid is then obtained in a downstream distillation.

A disadvantage of these processes is the use of expensive
10 oxidants which lead to heavy-metal-containing distillation residues, the disposal of which is problematic. In addition, toxic products can be formed, for example formic acid from formaldehyde, in such oxidation processes.

15 The object was therefore to find an inexpensive process which makes possible as complete as possible a removal of aldehydes and acetals from industrially prepared acetic acid, in which there are no disposal problems and no toxic products are formed.

20 Surprisingly, the object could be achieved according to the invention by reacting the industrially prepared acetic acid in the presence of a Brönstedt acid and 0.05 to 1% by weight of water and, if required, of 3 to 10 equivalents, calculated on aldehyde and acetal, of a
25 high-boiling polyhydric alcohol having the general

structural member



in which n is an integer from 0 to 3 and m is an integer greater than 3, at temperatures of 50 to 118°C for a period of 1 to 5 hours, and then isolating the pure
5 acetic acid from the reaction product by fractional distillation.

The process of the invention can, furthermore, if desired, have the feature that

- a) the Brönstedt acid used is a substance selected from
10 the group consisting of sulfuric acid, methanesulfonic acid, toluenesulfonic acid or phosphoric acid in an amount of 0.005 to 0.05 mol/l of contaminated acetic acid;
- b) the high-boiling polyhydric alcohol used is a sub-
15 stance selected from the group consisting of poly(vinyl alcohol), cane sugar and dextrose, starch or cellulose.

The industrially prepared acetic acid is advantageously reacted with an excess of the high-boiling polyhydric
20 alcohol in order to ensure as complete as possible a removal of the aldehydes and acetals.

A polyhydric alcohol which is obtained by hydrolysis of poly(vinyl acetate) in methanol can advantageously be used.

If only a partial purification of the industrial acetic acid is desired, the addition of the high-boiling polyhydric alcohol can be dispensed with. Example 1 shows the cleaning effect without addition of high-boiling polyhydric alcohol.

The Examples 1, 2 and the comparative example were carried out with an industrially prepared acetic acid which contained the following impurities:

	<u>Acetic acid content</u>	<u>99.6</u>	<u>[% by weight]</u>
	Water	0.036	[% by weight]
	Formaldehyde	57	[ppm]
15	Acetaldehyde	1.8	[ppm]
	Methyl acetate	59	[ppm]
	Ethyl acetate	151	[ppm]
	Isopropyl acetate	40	[ppm]
	Methoxymethyl acetate	130	[ppm]
20	Chromic acid test, according to Schering	80	[g of CrO ₃ % kg]
	(% kg denotes "per 100 kg")		

The invention is described in more detail by means of the examples.

Example 1 (without addition of polyhydric alcohol)

5 kg of industrially prepared acetic acid, together with 3.5 g of water and 5 g of methanesulfonic acid, were placed in the evaporator of a vapor baffle plate column having 20 plates and were refluxed for 3 h at an overhead pressure of 350 mbar. The mixture was then fractionally distilled at an overhead pressure of 350 mbar with a reflux ratio decreasing towards the end (10:1 to 2:1). By combining individual fractions, in total, after a low-boiling first runnings of 0.54 kg (including cold trap product), 1.68 kg of acetic acid (33.6% by weight of starting material) were obtained having a chromic acid test of 21 g of CrO_3 % kg and 2.73 kg of acetic acid (54.6% by weight of starting material) having a chromic acid test < 10 g of CrO_3 % kg.

Example 2 (with addition of polyhydric alcohol)

5 kg of industrially prepared acetic acid, together with 3.5 g of water, 5 g of methanesulfonic acid and 0.9 g of MOWIOL® 10-74 (10-fold equivalent excess calculated on aldehyde and acetal), were refluxed in a 6 l glass flask having an attached 20-plate vapor baffle plate column at an overhead pressure of 350 mbar for 3 hours at a bottom temperature of 87.5°C. The fractional distillation at a reflux ratio of 10:1 yielded 350 g of an aqueous first runnings having a chromic acid test of 216 g of CrO_3 % kg. At bottom temperatures between 90°C and 112°C (89°C

to 90°C on plate 10 of the column, overhead temperature 87°C) with decreasing reflux ratio (10:1 to 2:1), 4520 g of acetic acid were then obtained having a chromic acid test of 7 g of CrO₃ % kg (DAB 10 quality: < 32 g of CrO₃ % kg) and the analysis listed in Table 1 was obtained. This represents 90% of the acetic acid used. A further 23 g are located in the distillation cold trap, the residue remains as distillation bottom product.

TABLE 1

10		Purified acetic acid	
	Acetic acid content	99.8	[%]
	Water	0.18	[%]
	Formaldehyde	< 10	[ppm]
	Acetaldehyde	0.2	[ppm]
15	Methyl acetate	< 10	[ppm]
	Ethyl acetate	< 10	[ppm]
	Isopropyl acetate	< 10	[ppm]
	Methoxymethyl acetate	< 10	[ppm]
	Chromic acid test,		
20	according to Schering	7	[g of CrO ₃ % kg]

Comparative Example (purification by distillation only)

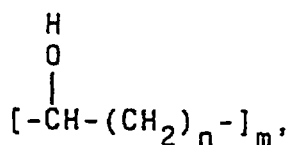
500 g of industrially prepared acetic acid were placed in the evaporator of a column having 30 plates. Under complete reflux conditions, the evaporator contents were heated to 85°C at an overhead column pressure of

230 mbar. As soon as the column was in equilibrium, fractional distillation was carried out at a reflux of 6:1. After a first runnings of 83 g was taken off, a fraction was obtained of 167 g having a chromic acid test
5 of < 32 g of CrO_3 % kg. The following 139 g of distillate, with a chromic acid test of < 10 g of CrO_3 % kg, had a further improved purity. Subsequently to this fraction, a further 83 g were obtained having a chromic acid test of < 32 g of CrO_3 % kg. 27 g remained as bottom
10 product. In total, 50.0% of the acetic acid used were obtained having a chromic acid test < 32 g of CrO_3 % kg and 28.0% of the acetic acid used were obtained having a chromic acid test < 10 g of CrO_3 % kg.



Patent Claims

1. A process for the removal of aldehydes and acetals from industrially prepared acetic acid, which comprises reacting the contaminated acetic acid in the presence of a Brönstedt acid and 0.05 to 1% by weight of water and, if required, of 3 to 10 equivalents, calculated on aldehyde and acetal, of a high-boiling polyhydric alcohol having the general structural member



in which n is an integer from 0 to 3 and m is an integer greater than 3, at temperatures of 50 to 118°C for a period of 1 to 5 hours, and then isolating the pure acetic acid from the reaction product by fractional distillation.

2. The process as claimed in claim 1, wherein the Brönstedt acid used is a substance selected from the group consisting of sulfuric acid, methanesulfonic acid, toluenesulfonic acid or phosphoric acid in an amount of 0.005 to 0.05 mol/l of contaminated acetic acid.

3. The process as claimed in claim 1, wherein the high-boiling polyhydric alcohol used is a substance



selected from the group consisting of poly(vinyl alcohol), cane sugar, dextrose, starch or cellulose.