

Description

The present invention relates to a process for removing iodide derivatives, eg alkyl iodides and the like, from acetic acid and/or acetic anhydride. In particular the present invention is suited to purifying acetic acid and/or acetic anhydride prepared by the rhodium catalysed, methyl iodide promoted carbonylation of methanol and/or methyl acetate.

It is known that a problem associated with acetic acid and/or acetic anhydride produced by carbonylation of methanol and/or methyl acetate in the presence of a rhodium/methyl iodide catalyst system is that, even after distillation, the acetic acid and/or acetic anhydride frequently contains small amounts of iodide impurities. Whilst the exact nature of these compounds is not known for certain, they probably comprise a mixture of methyl iodide and other higher alkyl iodides e.g. hexyl iodide. Such impurities are particularly troublesome since they poison many of the catalysts which are employed in subsequent chemical conversions of the acetic acid and/or acetic anhydride. A case in point is the catalysts used to prepare vinyl acetate from ethylene and acetic acid which are extremely sensitive to such impurities.

Several methods of removing iodine and its compounds from acetic acid and/or acetic anhydride are known. GB 2112394A, for example, teaches the use of anion exchange resins, whilst US 4615806 and EP 296584 disclose the removal of iodide impurities from non-aqueous organic media such as acetic acid by the use of a silver or mercury containing macroreticular strong acid cation exchange resin such as Amberlyst 15 (Amberlyst is a Registered Trade Mark).

A problem, however, arises when the silver loaded macroreticular resins described in US 4615806 and EP 296584 are used over a long period of time. This problem is particularly significant when preparing products with very low levels of iodide (e.g. less than 20 parts per billion (ppb)) from feeds containing up to 10 parts per million (ppm). In such cases it is found that, whilst silver loaded macroreticular resins are initially very effective, their efficiency declines significantly over a relatively short time. In practice this decline in efficiency is usually such as to render the resin unusable long before all the silver on it has been utilised.

It has now been found that this problem can be overcome by the use of certain ion-exchange resins intermediate in character between macroreticular resins on the one hand and gel resins on the other. Such resins, hereafter termed mesoporous resins, are characterised by a relatively low degree of crosslinking and by the fact that, whilst they have nearly gel structures when dried from a polar solvent such as water, their pore structure can be preserved if prior to drying the water is replaced by a solvent of lower polarity such as methanol.

According to the present invention there is provided a process for removing iodide derivatives from liquid acetic acid and/or acetic anhydride which comprises contacting the liquid acetic acid or acetic anhydride with a strong acid cation exchange resin having from 4% to 12% crosslinking, a surface area in the proton exchanged forms of less than $10\text{m}^2\text{g}^{-1}$ after drying from the water wet state and a surface area of greater than $10\text{m}^2\text{g}^{-1}$ after drying from a wet state in which water has been replaced by methanol, said resin having at least one percent of its active sites converted to the silver form.

The process of the present invention is particularly suited to reducing the levels of iodide derivatives, eg C_1 to C_{10} alkyl iodides, in the acetic acid or acetic anhydride from levels of up to 10 ppm down to levels of less than 10 ppb, most preferably to reducing the iodide content from 500ppb to less than 5ppb.

Mesoporous resins are defined as styrene/divinyl benzene copolymers having from about 4 to about 12% preferably from 6 to 10% crosslinking. Such resins are further characterised in that when dried from the water wet state in the proton exchanged form they have a surface area of less than $10\text{m}^2\text{g}^{-1}$ preferably less than $8\text{m}^2\text{g}^{-1}$ whilst when dried from a wet state in which water has been replaced by methanol, they have a surface area greater than $10\text{m}^2\text{g}^{-1}$ preferably greater than $15\text{m}^2\text{g}^{-1}$. The surface areas given above are those measured by the nitrogen BET method and the methods used to effect drying are those referred to as METHODS A and B below.

Particularly preferred examples of mesoporous resins are those materials which are sold under the trade names Purolite C145, Purolite CT145, Bayer K2441 and Bayer K2411.

The amount of silver present on the resin to be used is suitably such that at least one percent of the active sites which can be occupied by metal cations are loaded, preferably 10 to 90 percent of the sites, most preferably 30 to 70 percent. The silver-loaded resins can be prepared by ion-exchange or impregnation techniques, known in the art. A preferred method is that described in EP 296584 involving slurrying a sample of the resin in the proton exchanged form with silver oxide in water and thereafter treating the slurry with a carboxylic acid preferably acetic acid.

The process of the present invention is suitably carried out by passing liquid acetic acid or acetic anhydride contaminated with the iodide derivatives through a fixed bed of the resin at a predetermined rate. Preferably the resin bed is graded by backflushing before use. The feed rate used will depend on a number of variables including the amount of iodide impurities in the acetic acid or acetic anhydride, the degree of acid or anhydride purity required and the particular resin employed. Typical flow rates are in the range 0.5 to 50 bed volumes per hour, preferably 5 to 15. Optimum flow rates will depend upon temperature and can be readily determined.

The temperature at which the process is carried out must be high enough to prevent acetic acid or acetic anhydride from freezing at one extreme or boiling at the other. Typical ranges are 20 to 120°C preferably 25 to 100°C . Whilst in general it is desirable to operate at as high a temperature as possible, in order to effect maximum removal, it may, in certain circumstances for reasons of economy, be desirable to operate at a lower temperature and modify one of the

other process variables to reach the target level of iodide removal. The stability of the resins may also impose an upper limit on the operating temperature.

The process of the present invention will now be illustrated by the following Examples.

5 Example 1

Purolite C145 (Mesoporous Resin)

112.5 g (143 ml) of the wet resin (as supplied) was charged to a 500 ml pot equipped with a 5 cm diameter PTFE
 10 impeller. Distilled water (100 ml) was added and the mixture stirred at 60 rpm for 15 minutes. The water was then drawn off and another 100 ml of distilled water added. This procedure was then repeated (total washings 3 x 100 ml water). Silver (I) oxide (9.5 g-ex Aldrich) was added together with enough distilled water to cover the solids (ca 100 ml). The mixture was stirred at 60 rpm for 1 h at room temperature to thoroughly mix the reactants. Acetic acid (75 ml) was then
 15 added and the mixture heated to 50°C for 3 h whilst being stirred at 60 rpm. The resin was filtered off, washed with acetic acid (2 x 150 ml) and dried under flowing air.

Example 2

Bayer K2411 (Mesoporous Resin)

20 The method above was repeated using Bayer K2411 resin 125.0 g (174 ml) and silver oxide (9.5 g).

Comparative Test A

Amberlyst 15 (Macroreticular Resin)

25 The method above was repeated using Amberlyst 15 resin 87.0 g (100 ml) and silver oxide (7.7 g).

Comparative Test B

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Amberlite IR120 (Gel Resin)

35 The method above was repeated using Amberlite IR120 resin 70 g (82 ml) and silver oxide (6.9 g).

The products of Examples 1 and 2 and Comparative Tests A and B were analysed for silver. The results are shown in Table 1 below.

TABLE 1

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Resin	*Ag (%w/w)	H+ Exchange Capacity (mol/L _{resin})	% of Site Silver Exchanged
Purolite C145	12.5	1.6	35.8
Bayer K2411	10.2	1.25	37.7
Amberlyst 15	11.8	1.8	33.5
Amberlite IR120	10.5	1.95	37.2

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* Resins predried in oven at 100°C for ½ hr prior to analysis.

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Surface Area Measurements on Dry Resins

a. Methods for Drying the Resin

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METHOD A - Drying of Resin from Water Wet State

A 100 ml sample of the water wet resin as supplied was heated at 105°C to achieve a final pressure of ca 0.5 mbar of mercury after 4 hours.

METHOD B - Drying of Resin from Methanol Wet State

A 100 ml sample of the water wet resin was washed on a coarse sinter with seven volumes of methanol (approx 5-10 minutes). Thereafter the methanol wet resin was heated to 50°C at a pressure of 20mm of mercury for 30 minutes and then at 105°C to achieve a final pressure of ca 0.5 mbar of mercury after 4 hours.

b. Surface Area Measurements

Methods A and B were applied to samples of the resins Purolite C145 (mesoporous) Amberlyst 15 (macroreticular), Bayer K2411 (mesoporous) and Amberlite IR 120 (Gel).

The products of these experiments were then subjected to N₂ BET to measure their surface areas.

TABLE 2

Resin	Type	Surface Area by N ₂ BET (m ² /g)	
		Drying Method A	Drying Method B
Purolite C145	Mesoporous	7 ± 1	20 ± 1
Amberlyst 15	Macroreticular	41 ± 1	44 ± 1
Bayer K2411	Mesoporous	<5	20 ± 1
Amberlite IR120	Gel	<5	<5

General Procedure for Purifying Acetic Acid

25 mls of the silver loaded resin was charged to a column (1 cm diameter) containing acetic acid. The resin bed was then backflushed to remove any fines and to classify the resin particles according to size. Acetic acid dosed with 60 ppm iodide (added as hexyl iodide) was pre-heated to 43°C and passed downflow through the resin bed heated to 43°C. The resin bed was fitted with a weir system to ensure that it operated liquid full. Samples of the treated acetic acid were collected at intervals and analysed for iodide by neutron activation analysis.

Using the procedure described above silver loaded versions of the resins were tested as follows:

- Example 3 - Bayer K2411 (Mesoporous)
- Comparative Test C - Amberlyst 15 (Macroreticular)
- Example 4 - Purolite C145 (Mesoporous)
- Comparative Test D - Amberlite IR120 (Gel).

The results given in Table 3 below show that under equivalent conditions the two mesoporous resins (Purolite C145 and Bayer K2411) are superior to both Amberlyst 15 (macroreticular resin) and Amberlite IR120 (gel resin) in terms of

lifetime.

TABLE 3

Hours on Stream	Bayer K2411		Amberlyst 15		Purolite C145		Amberlite IRI20	
	I in Product (ppb by NAA)	% I removed	I in product (ppb by NAA)	% I removed	I in product (ppb by NAA)	% I removed	I in product (ppb by NAA)	% I removed
3							59000	-
11			13.6	99.98			62000	-
12							60500	-
13		99.98				99.98		
16							60000	-
20								
21	40	99.93						
24								
27			13.9	99.98				
31			22.0	99.96				
32								
33	31	99.95			37.0	99.94		
40							60000	-
41	52	99.91				99.98		
43			81.2	99.86				
59			601.0	99.00				
60					22.0	99.96		
61	168	99.72	1192.0	98.01				
67					49.9	99.92		
68								
69	232	99.61						
77	516	99.14						
79			3273.0	94.54				
80					174.0	99.71		
92					714.0	98.81		
95			8770.0	85.36	2455.0	95.90		
104								
105	7140	88.08	14400.0	75.96	4526.0	92.44		
107								
116			21000.0	64.94				
119			33500.0	44.07				
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Claims

1. A process for removing iodide derivatives from liquid acetic acid and/or acetic anhydride which comprises contacting the liquid acetic acid or acetic anhydride with a strong acid cation exchange resin having from 4% to 12% crosslinking, a surface area in the proton exchanged form of less than $10\text{m}^2\text{g}^{-1}$ after drying from the water wet state and a surface area of greater than $10\text{m}^2\text{g}^{-1}$ after drying from a wet state in which water has been replaced by methanol, said resin having at least one percent of its active sites converted to the silver form.
2. A process as claimed in claim 1 wherein the strong acid cation exchange resin has from 6 to 10% crosslinking.
3. A process as claimed in claim 1 or claim 2 wherein the strong acid cation exchange resin has a surface area of less than $8\text{m}^2\text{g}^{-1}$ after drying from the water wet state and a surface area of greater than $15\text{m}^2\text{g}^{-1}$ after drying from a wet state in which water has been replaced by methanol.
4. A process as claimed in any one of the preceding claims wherein from 10 to 90 percent of the active sites of the strong acid cation exchange resin are converted to the silver form.
5. A process as claimed in claim 4 wherein from 30 to 70 percent of the active sites of the strong acid cation exchange resin are converted to the silver form.
6. A process as claimed in any one of the preceding claims wherein the liquid acetic acid and/or acetic anhydride used as feedstock contains up to 500 parts per billion of the iodide derivatives.
7. A process as claimed in any one of the preceding claims wherein contact between the acetic acid and/or acetic anhydride and the strong acid cation exchange resin is achieved by passing the acetic acid and/or acetic anhydride through a fixed bed of the strong acid cation exchange resin.
8. A process as claimed in claim 7 wherein the fixed bed of the strong acid cation exchange resin is graded by back-flushing before use.
9. A process as claimed in either claim 7 or claim 8 wherein the flow rate of acetic acid and/or acetic anhydride through the fixed bed is in the range 5 to 15 bed volumes per hour.

Patentansprüche

1. Verfahren zur Entfernung von Iodid-Derivaten aus flüssiger Essigsäure und/oder aus Essigsäureanhydrid, welches das In-Kontakt-bringen der flüssigen Essigsäure oder des Essigsäureanhydrids mit einem stark sauren Kationenaustauscherharz mit von 4 % bis 12 % Vernetzung, einer inneren Oberfläche in der Protonenausgetauschten Form von weniger als $10\text{m}^2\text{g}^{-1}$ nach dem Trocknen aus dem wasserfeuchten Zustand und einer inneren Oberfläche von größer als $10\text{m}^2\text{g}^{-1}$ nach dem Trocknen aus dem feuchten Zustand, in welchem Wasser durch Methanol ersetzt worden ist, umfaßt, wobei das Harz zumindest ein Prozent seiner aktiven Zentren in die Silberform umgewandelt enthält.
2. Verfahren nach Anspruch 1, worin das stark saure Kationenaustauscherharz von 6 bis 10 % Vernetzung aufweist.
3. Verfahren nach einem der Ansprüche 1 oder 2, worin das stark saure Kationenaustauscherharz eine innere Oberfläche von weniger als $8\text{m}^2\text{g}^{-1}$ nach dem Trocknen aus dem wasserfeuchten Zustand und eine innere Oberfläche von größer als $15\text{m}^2\text{g}^{-1}$ nach dem Trocknen aus einem feuchten Zustand, in welchem Wasser durch Methanol ersetzt worden ist, aufweist.
4. Verfahren nach einem der vorstehenden Ansprüche, worin von 10 bis 90 Prozent der aktiven Zentren des stark sauren Kationenaustauscherharzes in die Silberform umgewandelt worden sind.
5. Verfahren nach Anspruch 4, worin von 30 bis 70 Prozent der aktiven Zentren des stark sauren Kationenaustauscherharzes in die Silberform umgewandelt sind.
6. Verfahren nach einem der vorstehenden Ansprüche, worin die als Ausgangsmaterial eingesetzte flüssige Essigsäure und/oder das Essigsäureanhydrid bis zu 500 Teile pro Billion der Iodid-Derivate enthalten.

7. Verfahren nach einem der vorstehenden Ansprüche, worin der Kontakt zwischen der Essigsäure und/oder dem Essigsäureanhydrid und dem stark sauren Kationenaustauscherharz durch Hindurchleiten der Essigsäure und/oder des Essigsäureanhydrids durch ein Festbett des stark sauren Kationenaustauscherharzes erreicht wird.
8. Verfahren nach Anspruch 7, worin das Festbett des stark sauren Kationenaustauscherharzes durch Rückspülung vor der Verwendung eingestuft ist.
9. Verfahren nach einem der Ansprüche 7 oder 8, worin die Fließrate der Essigsäure und/oder des Essigsäureanhydrids durch das Festbett im Bereich von 5 bis 15 Bettvolumina pro Stunde liegt.

Revendications

1. Procédé pour éliminer des dérivés consistant en iodures à partir de l'acide acétique liquide et/ou de l'anhydride acétique liquide, qui comprend la mise en contact de l'acide acétique liquide ou de l'anhydride acétique liquide avec une résine échangeuse de cations, du type acide fort, ayant une réticulation de 4 % à 12 %, une surface spécifique sous la forme ayant subi un échange de protons inférieure à $10 \text{ m}^2\text{g}^{-1}$ après séchage à partir de l'état imprégné d'eau et une surface spécifique supérieure à $10 \text{ m}^2\text{g}^{-1}$ après séchage à partir d'un état humide dans lequel l'eau a été remplacée par le méthanol, ladite résine ayant au moins 1 % de ses sites actifs transformé en la forme chargée en argent.
2. Procédé suivant la revendication 1, dans lequel la résine échangeuse de cations, du type acide fort, a une réticulation de 6 à 10 %.
3. Procédé suivant la revendication 1 ou la revendication 2, dans lequel la résine échangeuse de cations, du type acide fort, a une surface spécifique inférieure à $8 \text{ m}^2\text{g}^{-1}$ après séchage à partir de l'état imprégné d'eau et une surface spécifique supérieure à $15 \text{ m}^2\text{g}^{-1}$ après séchage à partir d'un état humide dans lequel l'eau a été remplacée par le méthanol.
4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel 10 à 90 % des sites actifs de la résine échangeuse de cations, du type acide fort, sont transformés en la forme chargée en argent.
5. Procédé suivant la revendication 4, dans lequel 30 à 70 % des sites actifs de la résine échangeuse de cations, du type acide fort, sont transformés en la forme chargée en argent.
6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'acide acétique liquide et/ou l'anhydride acétique liquide utilisés comme charge d'alimentation contiennent jusqu'à 500 parties par billion des dérivés consistant en iodures.
7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le contact entre l'acide acétique et/ou l'anhydride acétique et la résine échangeuse de cations du type acide fort, est réalisé en faisant passer l'acide acétique et/ou l'anhydride acétique à travers un lit fixe de la résine échangeuse de cations, du type acide fort.
8. Procédé suivant la revendication 7, dans lequel le lit fixe de la résine échangeuse de cations, du type acide fort, est calibré par rinçage à contre-courant avant utilisation.
9. Procédé suivant la revendication 7 ou la revendication 8, dans lequel le débit d'acide acétique et/ou d'anhydride acétique à travers le lit fixe est compris dans l'intervalle de 5 à 15 volumes de lit par heure.

