

## DESCRIPTION

OPERATING METHOD IN REMOVING IODINE  
COMPOUNDS CONTAINED IN ORGANIC MEDIUM

## Field of the Invention

The present invention relates to an operating method in removing iodine compounds from an organic medium by means of ion exchange resins, specifically to an operating method in removing iodine compounds contained in acetic acid or a mixture of acetic acid and acetic anhydride by contacting them with a cation exchange resin converted to a mercury form or a silver form.

## Description of the Related Art

Various methods for removing iodine compounds from organic media are disclosed. Particularly iodine compounds contained in acetic acid can not completely be removed in some cases even by distillation, and in the case where acetic acid is chemically changed to produce, for example, vinyl

acetate, there is brought about the serious problem that contamination is caused by iodine compounds, which results in shortening a life of a metal catalyst. Accordingly, many removing methods are investigated.

Methods in which iodine compounds are removed by contacting them with strong acid cation exchange resins in which active sites are converted to a silver form or a mercury form are disclosed as a method for removing iodine compounds from acetic acid or a mixture of acetic acid and acetic anhydride. It is reported in, for example, JP-B 5-21031 that it is effective to use a macroreticular strong acid cation exchange resin in which at least 1 % of the active sites is converted to a silver form or a mercury form. It is described therein that the cation exchange resin can be used at temperatures falling in a range of from a solidifying point of an organic liquid up to a decomposition temperature of the resin, that is, 17 to 100°C. On the other hand, however, it is described that temperatures are not important, and

not only descriptions on the temperatures are not found in the examples, but also nothing is described about the operation of the running temperatures.

It is disclosed in JP-A 4-282339 that a silver-containing meso-porous resin having a cross-linking degree of 6 to 10 % can be used for removing iodine compounds. The typical temperatures fall in a range of 20 to 120°C, and the temperature actually used in the examples is 43°C. The temperatures used in JP-A 5-301839 fall in a range where the liquids are maintained, that is, 20 to 120°C, and the temperature actually used in the examples is 79°C.

It is reported in JP-B 7-14488 that a method using a cross-linked macroreticular resin obtained by combining silver ions with active sites thereof by ion exchange is effective. It is described that the suitable temperatures fall in a range of from the solidifying point, 17°C, of acetic acid up to the boiling point, 118°C, of acetic acid and that the resin has a decomposition temperature of 150°C

or lower. Further, it is described that since the corrosion rate is increased at high temperatures, the removal should be carried out at as low temperatures as possible taking the desired removing rate into consideration. The temperatures are 20°C in the examples and 40°C in the comparative examples. However, the reaction rate is inferior at low temperatures, and therefore a removing efficiency of iodine compounds and a usage of silver are deteriorated.

Follow-up experiments for the examples described in these methods have been carried out by the present inventors to confirm the problems that as a matter of fact, silver is dissolved to some extent in acetic acid or a mixture of acetic acid and acetic anhydride obtained after contacting with the ion exchange resins due to a nature of an ion exchange equilibrium of silver ion in an acid or because of an instability of the resins attributable to temperatures to not only bring about the deterioration of the quality but also cause a deterioration in the silver usage. This is

notable as the temperatures are elevated. Silver runs off markedly, for example, at 79°C, and therefore such temperature should not be employed.

It is reported in JP-B 5-21031 that it is convenient to put an ion exchange resin bed which is not yet converted to a silver form after an ion exchange resin bed which has been converted to a silver form.

However, there are the problems that a large quantity of the ion exchange resins and the long resin-packed bed are required in order to recover a low concentration of silver and that the facilities cost a lot and the recovering cost is required, which raise the total cost.

Further, as described above, a reaction mechanism of iodine compounds with carried silver has not yet been analyzed, and a reaction rate and a removing performance in the insides of macroreticular resins and meso-porous resins are not yet satisfactory.

#### Summary of the Invention

An object of the present invention is to

provide an operating method which can reduce an amount of silver or mercury dissolved in a solution after contact and can improve a usage of silver or mercury without installing new treating facilities in a process for removing iodine compounds contained in an organic medium, particularly acetic acid or a mixture of acetic acid or acetic anhydride by contacting them with a cation exchange resin in which at least 1 % of active sites is converted to a silver form or a mercury form.

The present inventors have kinetically investigated a mechanism to remove iodine compounds in a process for removing iodine compounds contained as impurities in an organic medium, particularly acetic acid and a mixture of acetic acid or acetic anhydride by contacting them with an ion exchange resin in which at least 1 % of active sites is converted to a silver form or a mercury form. As a result thereof, they have noticed that a diffusion resistance in the pores of the resin is dominant and found that the diffusion rate and the reaction rate can be raised by elevating the

operating temperatures to increase notably a removing efficiency and a life of the resin. Further, they have found the problems that the run-off of silver or mercury due to an ion exchange equilibrium and the run-off of silver or mercury and sulfate radicals due to the deterioration of the resin are increased. The present inventors have found from these matters that the deterioration of the resin and the run-off of silver or mercury can be suppressed to the lowest level, and a removing efficiency and a life of the resin and a usage of silver or mercury can markedly be raised by contacting the organic medium containing iodine compounds with the ion exchange resin at relatively low temperatures in the beginning of the operation to maintain the deterioration of the resin and a run-off amount of silver or mercury at low levels and then elevating the temperature in stages when alkyl iodide such as hexyl iodide is about to be or has been detected in the vicinity of the exit of the resin bed, and thus the present invention has been completed. That is,

the present invention relates to an operating method in which an amount of silver or mercury dissolved in a solution obtained after contact can easily be reduced, the iodine compounds can most efficiently be removed and the usage of silver and mercury can be improved by carrying out the operation while elevating the temperature in stages.

The invention is directed to a process for removing iodine compounds from an organic medium, which comprises the step of bringing the organic medium into contact with a cation exchange resin in which at least 1 percent of active sites thereof have been changed to silver or mercury, while elevating the contacting temperature step by step or gradually in a continuous way.

It is preferable to elevate the temperature by 1 to 70 degree C, more preferably by 2 to 25 degree C, in particular by 3 to 15 degree C. The temperature may be elevated continuously at a low rate, for example, 1 to 70 degree C per year, more preferably by 2 to 25 degree C per year, in particular by 3 to 15 degree C per year. It may be elevated step by

step.

The product mixture of acetic acid may be taken out of a distillation column and cooled down to a given temperature before this treatment with a cation exchange resin. When the temperature of the ion exchange resin bed is higher than that of the product mixture, this may be heated to a given one.

The iodine-removing step can be conducted until the ion exchange resin has reached the saturation (break through point).

#### Detailed Description of the Invention

The present invention shall specifically be explained below.

The ion exchange resin used in the present invention is preferably a cation exchange resin comprising a sulfonated copolymer of styrene and divinylbenzene.

A method for converting the ion exchange resin to a silver form or a mercury form is not particularly important, and any silver salts can be used as long as they have a suitable solubility in water or a non-aqueous organic medium. Silver

oxide, silver acetate and silver nitrate are typical examples thereof. A required amount of silver is more than an equivalent as that of the iodine compounds to be removed in terms of a mole ratio.

An average pore diameter of the ion exchange resin is preferably 100 angstrom or more, more preferably 600 angstrom or more.

The organic medium containing the iodine compounds includes organic acid, alcohol and ester. In particular, the operating method of the present invention is suited for the removal of iodine compounds contained in acetic acid or a mixture of acetic acid and acetic anhydride. More specifically, it is suited for the removal of iodine compounds contained in acetic acid or a mixture of acetic acid and acetic anhydride obtained by reacting at least one selected from methanol, methyl acetate and dimethyl ether with carbon monoxide or a mixture of carbon monoxide and hydrogen in the presence of a catalyst system containing a rhodium compound, methyl iodide and

alkaline metal iodide as a cocatalyst. The present invention shall not be restricted to the removal of halides contained in the organic medium and can be applied to the removal of halides contained in water or an aqueous solution.

The iodine compounds include alkyl iodides having a carbon number of up to about 10 such as hydrogen iodide, methyl iodide, ethyl iodide, propyl iodide, butyl iodide, pentyl iodide, hexyl iodide, heptyl iodide and octyl iodide, and a mixture thereof. The operating method of the present invention is effective as well to the removal of inorganic iodides such as lithium iodide and iodine ions. Further, it is effective to the removal of halogens other than iodine, for example, chlorine including alkyl chlorides having a carbon number of up to about 10, inorganic chlorides and chlorine ions. An amount thereof is about 0.1 to 1000 ppb in terms of a concentration in a liquid.

In general, when ion exchange resins are industrially used, liquids to be treated is continuously passed through a packed bed in which

the resins are filled. However, the resins may be used batchwise or by a fluidized bed method. When they are used in a continuous flow system, such a flow rate and a bed volume per hour as reducing an influence exerted by a boundary diffusion resistance are generally employed, and the economically advantageous conditions may be employed according to the characteristics of the resins used and the kinds, characteristics and concentrations of the iodine compounds to be removed.

A lower limit of use temperatures of the ion exchange resins is 17°C which is the solidifying point of acetic acid, and an upper limit thereof is 120°C which is a heat resistant temperature of the resin. The temperatures exceeding 90°C bring about the deterioration of the resin which can not be ignored, and therefore the temperatures falling in a range of 20 to 90°C is preferably selected optionally. In a method for elevating the temperatures in stages, the operation is carried out preferably at relatively low temperatures of 17

to 35°C in the beginning of the operation to use the resin for removing the iodine compounds during a time expended until the resin bed is used to the maximum, that is, the saturation (arrives a break through point) while maintaining a run-off amount of silver or mercury to a low level. Then, the temperature is elevated to the second stage, for example, about 45°C to shorten a length of the adsorption band and a moving rate of the adsorption band. That is, the utilization is raised; the resin life which is the time expended until the saturation is extended; and the usage is improved. The more the temperature is elevated, the more this effect is improved, but the more the run-off loss amount of silver or mercury is increased as well. Accordingly, the temperature in the second stage is preferably elevated by about 10°C. At the temperature in the second stage, the resin bed is used for removing the iodine compounds while maintaining a run-off amount of silver or mercury at a low level until the resin bed is the saturation (break through point). Then, the

temperature is elevated to the third stage, for example, about 55°C to shorten a length of the adsorption band and a moving rate of the adsorption band to extend the resin life and raise the usage. Hereafter, the above procedures are repeated, whereby the deterioration of the resin and the run-off of silver or mercury can be minimized, and an efficiency of removing alkyl iodides, the resin life and a usage of silver or mercury can notably be improved.

In general, a stainless material is used in handling acetic acid and can be used at 120°C without having an anxiety of corrosion.

These methods are not restricted to cases using the ion exchange resins and can be applied to cases using industrially usable carriers, for example, alumina, silica, silica-alumina, zeolite and activated carbon carrying silver or mercury.

According to the present invention, the temperatures are elevated in stages to carry out the operation, whereby the deterioration of the resin and the run-off of silver or mercury can be

minimized, and an efficiency of removing alkyl iodides, the resin life and a usage of silver or mercury can notably be improved.

#### Examples

The present invention shall more specifically be described below with reference to examples, but the present invention shall not be restricted by these examples.

Iodine compounds contained in organic media shown in Comparative Example 1 and Examples 1 and 2 are removed by the following method.

Acetic acid containing 15 to 20 ppb of hexyl iodide is continuously contacted with a packed bed of a strong acid cation exchange resin carried on active sites with silver and having a macroreticular structure while maintaining prescribed temperatures. Acetic acid after contacting is taken out of a sampling port attached to the column by every fixed time to analyze a concentration of hexyl iodide by means of a gas chromatograph (ECD-GC) equipped with an electron capture type detector to confirm a removing state

thereof and analyze a silver concentration by atomic absorption analysis. The ion exchange resin used is Amberlist 15 in which 41 % of active sites is converted to a silver form, manufactured by Rohm & Haas Co., Ltd.. The column used has an inner diameter of 26 mm and a resin-packed height of 1600 mm. This column has sampling ports disposed at four spots.

#### Comparative Example 1

Concentrations of silver contained in an effluent in the beginning of the operation and the stable operation were determined, wherein acetic acid containing the iodine compounds was contacted with a packed bed of the ion exchange resin converted to a silver form at a flow rate of 12.8 bed volume per hour (1 bed volume is 616 ml). The experiments were carried out independently at operating temperatures of 28°C, 54°C and 70°C, respectively. The concentrations of silver contained in the effluents are shown in Tables 1 to 3. Hexyl iodide was not detected at the exit of the resin-packed bed.

In the case of 54°C which is higher by 26°C than 28°C, silver is dissolved in acetic acid after contacting in about four times as much amount as in the case of 28°C. In the case of 70°C which is higher by 42°C than 28°C, silver is dissolved in acetic acid after contacting in about eleven times as much amount as in the case of 28°C. That is, it can be found that the higher the operating temperature is, the more the loss of silver is increased.

Table 1

Concentration of silver contained in effluent

(operation temperature: 28°C)

|                        | elapsed<br>Time | Concentration<br>of silver(ppb) |
|------------------------|-----------------|---------------------------------|
| Beginning of operation | 816 hrs         | 12                              |
| Stable operation       | 3179 hrs        | 1.1                             |

Table 2

Concentration of silver contained in effluent

(operation temperature: 54°C)

|                        | elapsed<br>Time | Concentration<br>of silver(ppb) |
|------------------------|-----------------|---------------------------------|
| Beginning of operation | 620 hrs         | 43                              |
| Stable operation       | 1652 hrs        | 14                              |

Table 3

Concentration of silver contained in effluent  
(operation temperature: 70°C)

|  | elapsed<br>Time | Concentration<br>of silver (ppb) |
|--|-----------------|----------------------------------|
|  | 1206 hrs        | 130                              |

Example 1

The stable operation was carried out while contacting acetic acid containing iodine compounds with the ion exchange resin converted to a silver form at a temperature of 33°C and a flow rate of 7.2 bed volume per hour, and the temperature was then elevated to 43°C. The silver concentrations determined during the operation are shown below.

Table 4

Concentrations of silver and sulfate radical contained in effluent (temperature was varied during continuous operation )

|                                          | elapsed<br>Time          | Concentration<br>of silver | Concentra-tion of<br>sulfate radical |
|------------------------------------------|--------------------------|----------------------------|--------------------------------------|
| Beginning of<br>operation (33°C)         | 24 hrs<br>187 hrs        | 24 ppb<br>2.7 ppb          | 130 ppb<br>2 ppb                     |
| Stable<br>operation (33°C)               | 5683 hrs                 | 1.8 ppb                    | 1 ppb                                |
| after elevating<br>temperature<br>(43°C) | 5803 hrs<br>(total time) | 2.3 ppb                    | 4 ppb                                |

A marked run-off of silver is not observed even if the temperature is elevated from an intermediate stage of the operation.

Further, a usage of silver carried on the ion exchange resin was investigated based on a change in a concentration of hexyl iodide in the packed bed with lapse of time. As a result thereof, it has been found that an increase in the temperature by 10°C from 33°C to 43°C shortens a length of the absorption band by 0.83 time and a moving rate of the absorption band by 0.69 time, that is, raises the usage to extend the resin life by about 1.4 time.

Thus, the resin bed was used the removal of hexyl iodide at a low temperature of 33°C during a period until the resin bed is close to the saturation in the beginning of starting the operation, and then the temperature is elevated to 43°C, whereby a run-off loss amount of silver can be controlled to a low level, and the resin life can be extended.

Example 2

The stable operation was carried out while contacting acetic acid containing iodine compounds with the ion exchange resin converted to a silver form at a temperature of 28°C and a flow rate of 12.8 bed volume per hour, and the temperature was then elevated to 54°C. The silver concentrations determined during the operation are shown below.

Table 5

Concentrations of silver and sulfate radical contained in effluent (temperature was varied during continuous operation.)

|                                    | elapsed Time             | Concentration of silver | Concentration of sulfate radical |
|------------------------------------|--------------------------|-------------------------|----------------------------------|
| Beginning of operation (28°C)      | 816 hrs                  | 12 ppb                  | 8 ppb                            |
| Stable operation (28°C)            | 3179 hrs                 | 1.1 ppb                 | 1 ppb                            |
|                                    | 7485 hrs                 | 2.0 ppb                 | 1 ppb                            |
| after elevating temperature (54°C) | 8807 hrs<br>(total time) | 3.7 ppb                 | 1 ppb                            |

A marked run-off of silver is not observed even if the temperature is elevated from an intermediate stage of the operation.

Further, a usage of silver carried on the ion exchange resin was investigated based on a change

in a concentration of hexyl iodide in the packed bed by a lapse of time. As a result thereof, it has been found that a rise in the temperature to 54°C has extended the resin life by 2.1 times as compared with that in the case of 28°C. Further, a subsequent rise to 70°C has extended the resin life by 3.7 times as compared with that in the case of 28°C.

It has been found from the results summarized in Tables 1 to 3 that the earlier the stage of the operation is and the higher the temperature is, the more the run-off amount of silver is. Accordingly, a marked run off of silver can be reduced and a usage of silver carried on the ion exchange resin can be raised by carrying out an operating method in which the operation is carried out at relatively low temperatures in the beginning and the temperature is elevated when a contact of acetic acid containing the iodine compounds with the ion exchange resin converted to a silver form is stabilized.



### Claims

1. An operating method in removing iodine compounds from an organic medium by contacting them with a cation exchange resin in which at least 1 % of active sites is converted to a silver form or a mercury form, wherein the operation is carried out while elevating the temperatures in stages.
2. The method as claimed in Claim 1, wherein 1 to 100 % of the active sites is converted to a silver form or a mercury form.
3. The method as claimed in Claim 1, wherein the organic medium is acetic acid or a mixture of acetic acid and acetic anhydride.
4. The method as claimed in Claim 1, wherein the iodine compounds are selected from alkyl iodides.
5. The method as claimed in Claim 3, wherein acetic acid or a mixture of acetic acid and acetic anhydride is contacted with the cation exchange resin at temperatures of 17 to 120°C and a flow rate of 0.5 to 40 bed volume per hour.
6. The method as claimed in Claim 5, wherein acetic acid or a mixture of acetic acid and acetic



anhydride is contacted with the cation exchange resin at temperatures of 17 to 35°C in the beginning of the operation, and then the temperature is elevated in stages.

7. The method as claimed in Claim 1, wherein the iodine compound is at least one selected from the group consisting of methyl iodide and hexyl iodide.