



Specification

METHOD OF PURIFYING ACETIC ACID

Background of the Invention

Field of the Invention

The present invention relates to an industrial method for purifying acetic acid, particularly to a method for purifying acetic acid obtained by carbonylation of methanol.

Description of the Related Art

Acetic acid is a basic chemical employed as a starting material of each of, for example, acetic esters, acetic anhydride, vinyl acetate and terephthalic acid and thus employed in large quantity in the petrochemical, organic chemistry, pharmaceutical and agricultural chemical production, polymer chemistry and other industries.

Various industrial processes are known for producing acetic acid, which include, for example, oxidation of acetaldehyde, direct oxidations of hydrocarbons such as petroleum naphtha and butane, and carbonylation of methanol. Of these, the process in which acetic acid is produced by continuously carbonylating methanol with carbon monoxide (see Japanese Patent Publication-B No. 47-3334) is now widely employed as an industrial process for producing



acetic acid.

In recent years, reaction conditions and catalyst improvements have been studied in the above acetic acid production through carbonylation of methanol. For example, a process in which a catalyst stabilizer such as an iodide salt is added to the reaction system has been disclosed [see G.B. Patent Publication-A No. 2,146,637 (published on April 24, 1985)]. In Japanese Patent Publication-A No. 60-54334, it has been proposed to cause a relatively large amount of iodide ions to be present in a reaction fluid so as to lower the concentration of water in the reaction fluid, thereby minimizing the energy required to obtain purified dry acetic acid per unit quantity thereof and further omitting a purification process for obtaining acetic acid as a product [see European Patent Publication-A No. 573,189 (published on Dec. 8, 1993)].

Although the acetic acid produced by the carbonylation of methanol has a relatively high purity, it is known that the acetic acid contains a minute amount of reductive impurities evaluated by the potassium permanganate test conducted in accordance with JIS K 1351 [see European Patent Publication-A No. 322,215 (published on June 28, 1989)]. The potassium

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permanganate test is an important industrial test which acetic acid must pass when it is put in various practical uses as a product. Therefore, the removal of the above impurities leading to poor results in this test is of utmost importance.

The conventional purification methods for obtaining commercially available high-quality acetic acid capable of meeting the standards include, for example, (a) chemical addition method [for example, addition of an amine, a nonvolatile acid or the like as disclosed in Japanese Patent Publication-B No. 42-6243 (published on Mar. 14, 1967)] and (b) oxidant addition method [for example, addition of peracetic acid as disclosed in Japanese Patent Publication-B No. 48-30615 (published on Sep. 21, 1973)]. However, the above methods require the use of various additives, so that problems arise with respect to handling and aftertreatment. That is, not only at least simple distillation for separating the additives is further required but also there is a potential problem of the additives remaining in the acetic acid as a product. Especially, the oxidant addition method (b) has a potential danger of explosion attributed to a rapid reaction of peroxide remaining unreacted in separating the additives. Therefore, a purification method in



which no additives are added is desired.

While, in a distilling method, concentration of a minute amount of impurities to a considerable extent is required for minimizing acetic acid entrained in the separation and disposal of impurities to thereby suppress the purification loss of the acetic acid. Thus, the distillation column must have a considerably large number of plates and a considerably high reflux ratio. Consequently, a considerably large amount of thermal energy is to be consumed, thereby bringing about a problem of gravely pushing up the cost for purification. Therefore, a method of economically removing the above impurities is desired.

Disclosure of the Invention

Summary of the Invention

Under these circumstances, the present inventors have made extensive studies with respect to the purification of acetic acid which contains a minute amount of impurities composed of at least one component selected from among organoiodine compounds, metalloiodine compounds, iodide ions, unsaturated compounds and carbonyl compounds and which exhibits poor marks in the potassium permanganate test. As a result, a distilling method of the present invention



which ensures, without the addition of chemicals for separating the impurities, energy-saving economical purification for obtaining high-quality acetic acid which exhibits high marks in the potassium permanganate test, has been completed.

That is, the present invention relates to a method for purifying acetic acid containing at least one component selected from the group consisting of organoiodine compounds, metalloiodine compounds, iodide ions, unsaturated compounds and carbonyl compounds as an impurity, which comprises purifying the acetic acid with a distillation column having at least 30 plates by operating the distillation column under a pressure ranging from 40 to 760 mmHg at a reflux ratio of at least 4.

In other words, the present invention relates to a method of purifying acetic acid containing impurities composed of at least one component selected from among organoiodine compounds, metalloiodine compounds, iodide ions, unsaturated compounds and carbonyl compounds, characterized in that the purification is conducted in a distillation column having at least 30 plates operated under a pressure ranging from 40 to 760 mmHg at a reflux ratio of at least 4 to thereby obtain high-quality acetic acid as

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a product.

Although the present invention is in principle applicable to any acetic acid irrespective of its production process, it is advantageously applied especially to the product of carbonylation of methanol or the like performed in the presence of a metal catalyst such as a rhodium catalyst with the use of a cocatalyst of a halide such as an organic halide, as described in G.B. Patent Publication-A No. 1,233,121.

Further scope and applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

Detailed Description of the Invention

The production of acetic acid by carbonylation of methanol is performed in the following manner.

Methanol and carbon monoxide as the starting compounds are continuously charged in a reactor to conduct a reaction at a given temperature under a given pressure



as described in, for example, U.S. Patent No. 4,102,922 (published on July 25, 1978). One of the starting compound is not limited to methanol, but at least one of methyl acetate, dimethyl ether and methanol, a mixture of two or more of them or a mixture of at least one of the above compounds and water may be used. The reaction temperature ranges generally from about 150 to 250°C, preferably from about 180 to 220°C. The total reaction pressure is controlled so as to range from about 15 to 40 kg/cm²G in consideration for the partial pressures of carbon monoxide and hydrogen and the vapor pressures of the liquid components present in the reactor.

The rhodium catalyst which is employed in the carbonylation of methanol may take any form, as far as it can be converted into a complex soluble in the reaction fluid under the reaction conditions. In the reaction fluid, the rhodium concentration ranges from about 200 to 1000 ppm, preferably from about 300 to 600 ppm.

In the carbonylation of methanol, methyl iodide is used as a promoter and is contained in the reaction fluid in a concentration ranging from about 5 to 20% by weight, preferably from about 12 to 16% by weight.

The concentration of water in the reaction fluid

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is about 10% by weight or below, preferably from 1 to 5% by weight.

The carbonylation of methanol is continuously performed, so that methyl acetate formed by the reaction between methanol as the starting compound and acetic acid is present in the reaction fluid. The amount of methyl acetate is controlled so as to range from about 0.1 to 30% by weight, preferably from about 0.5 to 5% by weight. Also, acetic acid which is a product and a reaction solvent is present in the reaction fluid as a main component.

When the carbonylation of methanol is effected under low water content conditions, an iodide salt is added to the reaction fluid for the stabilization of the rhodium catalyst and as a cocatalyst. The above iodide salt is not particularly limited as long as it dissociates an iodide ion in the reaction fluid. Examples of the iodide salts include alkali metal iodides such as LiI, NaI, KI, RbI and CsI, alkaline earth metal iodides such as BeI_2 , MgI_2 and CaI_2 and aluminum-group metal iodides such as BI_3 and AlI_3 . The iodide salt is not limited to these metal iodides, and organic iodides may be used, which include, for example, quaternary phosphonium iodides (such as an adduct of tributylphosphine with methyl iodide or



hydrogen iodide and an adduct of triphenylphosphine with methyl iodide or hydrogen iodide) and quaternary ammonium iodides (such as adducts of tertiary amines with methyl iodide or hydrogen iodide, adducts of pyridines with methyl iodide or hydrogen iodide, adducts of imidazoles with methyl iodide or hydrogen iodide, and adducts of imides with methyl iodide or hydrogen iodide). Among them, alkali metal iodides such as LiI are preferred. The iodide salt is used, irrespective of the type of the iodide salt, in an amount of 0.07 to 2.5 mol/l, preferably 0.25 to 1.5 mol/l in terms of iodide ion, i.e., as a molar concentration of iodide ion contained in the reaction fluid.

The crude acetic acid thus formed is purified by an operation such as distillation for removing water. However, after the purification, the acetic acid generally contains, as an impurity, at least one component selected from the group consisting of organoiodine compounds, metalloiodine compounds, iodide ions, unsaturated compounds and carbonyl compounds, as described in European Patent Publication-A No. 322,215 (published on June 28, 1989). Examples of the organoiodine compounds include ethyl iodide, butyl iodide and hexyl iodide. Examples



of the unsaturated compounds include acetaldehyde, butyraldehyde, crotonaldehyde and 2-ethylcrotonaldehyde, and products formed by aldol condensation of these aldehydes. It is described in Japanese Patent Publication-A No. 1-211548 that the main components of the impurities are alkyl iodides, various unsaturated compounds such as crotonaldehyde, ethylcrotonaldehyde and 2-methyl-2-pentenal, and carbonyl compounds. These impurities present in minute amounts cause the mark of the potassium permanganate test of acetic acid to become poor, thereby lowering the commercial value and industrial availability of the acetic acid as a product.

The present inventors have been extensively studied with respect to the purification method of the above acetic acid. As a result, they have been found that the purification of the above acetic acid by the method of the present invention realizes economical conversion of the crude acetic acid to high-quality acetic acid which exhibits high marks in the potassium permanganate test.

That is, the present invention comprehends a methods of purifying acetic acid containing impurities composed of at least one component selected from among organoiodine compounds, metalloiodine compounds,



iodide ions, unsaturated compounds and carbonyl compounds in a process for producing acetic acid which comprises reacting methanol, a mixture of methyl acetate and water or a mixture of methyl acetate, methanol and water with carbon monoxide in a reaction medium containing a rhodium catalyst, water, acetic acid and methyl iodide, characterized in that the purification is conducted in a distillation column having at least 30 plates operated under a pressure ranging from 40 to 760 mmHg at a reflux ratio of at least 4 to thereby obtain high-quality acetic acid as a product.

Examinations of patent and other documents published heretofore have revealed that the distillation of acetic acid is carried out under the atmospheric or higher pressure [see G.B. Patent Publication-A No. 1,294,432 and U.S. Patent No. 4,029,553 (published on June 14, 1977)] and that no purification of acetic acid is effected under a reduced pressure. That is, the operation under the atmospheric or higher pressure has become like a matter of general knowledge in the purification of acetic acid by distillation.

In the present invention, the distillation is effected with a distillation column which can be



operated under reduced pressure. Any type of distillation columns customarily employed in separation and purification of solutions, including a packed column, a plate column and a combination thereof, may be used in the present invention as long as the following requirements are met. Generally, a plate column is employed for vacuum distillation.

In the present invention, the acetic acid to be purified which exhibits poor marks in the potassium permanganate test is fed into the distillation column at its middle and heated in a reboiler. Organic iodides, unsaturated compounds and carbonyl impurities, which may have boiling points lower than that of acetic acid, occasionally together with iodide ion impurities, are concentrated at the top of the column. Some impurities among them may be concentrated at the top of the column as an azeotropic mixture. On the other hands, iodide ion impurities, and organic iodides, unsaturated compounds and carbonyl impurities, which have boiling points higher than that of acetic acid, are concentrated at the bottom of the column.

For achieving the concentration and separation of the above impurities, the distillation column must have a large number of plates and a high reflux ratio



is necessitated. The distillation column has at least 30 plates, preferably at least 50 plates. The reflux ratio is at least 4, preferably at least 50.

The high reflux ratio inevitably requires a great amount of thermal energy in the reboiler. However, in the present invention, the distillation is performed under a reduced pressure, so that the boiling points of components in crude acetic acid are lowered. Accordingly, a great amount of thermal energy is not necessitated even when a high reflux ratio is employed. Therefore, in the purification method of the present invention, overhead steam, low-pressure waste steam and the like available from other distillation columns can be used as the heat source for the reboiler of the vacuum distillation column. Thus, little additional thermal energy is necessitated for the purification method of the present invention.

The operating pressure of the vacuum distillation column for use in the present invention ranges from 40 to 760 mmHg, of which an appropriate one can be selected by taking into account the temperature of the heat source for use in the reboiler. Especially, it is preferred that the operating pressure ranges from 40 to 400 mmHg, at which the temperature of bottoms is not higher the boiling point of water under the



atmospheric pressure to thereby widen the range of employable heat source.

The organic iodides, unsaturated compounds and carbonyl impurities, occasionally together with iodide ion impurities, which have been concentrated at the top of the column, are batchwise or continuously withdrawn in small quantity, and wholly or partially recycled to a carbonylation reactor for effective reutilization. On the other hand, the bottoms are batchwise or continuously withdrawn, if necessary, and recycled to the previous step. Alternatively, the components concentrated at the top and the bottom of the column may wholly or partially be disposed of outside the system in order to maintain the quality of acetic acid as a product.

In the present invention, the distillation is conducted at lower temperatures, so that the thermal conversion of acetic acid to, for example, acetic anhydride can be minimized, thereby achieving purification with minimized loss.

Acetic acid as a product is withdrawn in vaporous or liquid form from the distillation column at, for example, its second plate counted from the bottom.

Brief Description of the Drawings

Fig. 1a is a flow diagram showing a step of the



conventional acetic acid purification process and Fig. 1b is a flow diagram showing a step of the acetic acid purification process of the present invention.

Fig. 2 is a flow diagram showing the process according to the acetic acid purification method of the present invention.

In the above figures, reference numerals 1 to 5, 8 to 13, 16 to 20 and 23 to 28 are each a line, those of 6, 14, 21 and 29 are each a condenser, and those of 7, 15, 22 and 30 are each a reboiler.

Description of the Preferable Embodiment

One embodiment of the present invention will be described below with reference to Figs. 1a, 1b and 2 (Fig. 1a being a referential view) to thereby more clearly demonstrate the availability of the present invention.

Referring to Fig. 1b, the column B is a vacuum distillation column suitable for use in the present invention. Acetic acid to be purified which has poor marks in the potassium permanganate test is charged through a line 8 into the column B at its middle. Overhead steam output from the column B is led through a line 10 into a condenser 14, in which the steam is condensed. Part of the condensate is wholly recycled through a line 11 to a carbonylation reactor or



disposed off. Alternatively, part of the condensate is partially recycled through a line 11 to a carbonylation reactor and partially disposed off. The rest of the condensate formed in the condenser 14 is recycled through a line 12 to the column B as a reflux. Bottoms are withdrawn through a line 9. The bottoms are wholly recycled to the previous step or disposed off. Alternatively, the bottoms are partially recycled to the previous step and partially disposed off. The fluid withdrawn through a line 13 is used as a product acetic acid. Alternatively, the fluid is further purified by means of, for example, an ozone treatment.

Referring to Fig. 1a, the column A is a distillation column as described in U.S. Patent No. 4,029,553 (published on June 14, 1977) which is used for removing, through a line 2, a heavy fraction from acetic acid produced by carbonylation of methanol. This column A constitutes a step of the conventional acetic acid purification process and is operated under the atmospheric or higher pressure.

Acetic acid to be purified in the column A is charged through a line 1 into the column A at its middle. Overhead steam output from the column A is led through a line 3 into a condenser 6, condensed



there, and fed through a line 4 to the subsequent purification step. As shown in Fig. 1a, part of the flow from the condenser 6 is recycled through a line 5 to the column A as a reflux.

In the present invention, as shown in Fig. 2, the overhead steam led through a line 18 of the column A can be used as a heat source for a reboiler 30 of the column B. When the column A is operated at about 1.03 kg/cm², the temperature of the overhead is 118°C, which is satisfactory for use as the heat source for the column B. Therefore, in the present invention, acetic acid produced by the carbonylation of methanol can be purified into high-quality acetic acid which has high marks in the potassium permanganate test with little addition to the purification energy required in the conventional acetic acid purification process by the use of the overhead steam output from the distillation column A constituting a step of the conventional acetic acid purification process as the heat source for the reboiler of the vacuum distillation column B for use in the present invention.

Examples

The availability of the present invention will now be described with reference to the following examples which should not be considered to limit the



scope of the present invention.

Example 1

An acetic acid purification experiment was conducted with the use of a 50-plate Oldershaw distillation column (a type of plate column).

The pressure of the distillation column was controlled so as to be 400 mmHg at the top of the column, where the temperature was about 90°C. Acetic acid to be charged was fed at a flow rate of about 1.1 kg/hr to the 23rd plate counted from the bottom of the column. Purified acetic acid was withdrawn in vaporous form from a section very close to the bottom of the column. The distillation column was operated at a reflux ratio of about 150. Bottoms and overhead were continuously withdrawn outside the system at flow rates equal to about 1% and about 0.8% of the charge flow rate, respectively. Continuous operation under these conditions resulted in an improvement of the marks of the potassium permanganate test from 125 min of the charged acetic acid (this poor value being attributed to the inclusion of at least crotonaldehyde, ethylcrotonaldehyde and 2-methyl-2-pentenal) to at least 240 min of the purified acetic acid.

Example 2

Methanol was continuously carbonylated at 185°C



in the presence of carbon monoxide in a reaction medium consisting essentially of 14% by weight of methyl iodide, 8% by weight of water, 1.6% by weight of methyl acetate, 71% by weight of acetic acid, 5% by weight of lithium iodide and 400 ppm of rhodium, with the use of a continuous withdrawal autoclave (a carbonylation reactor), thereby producing acetic acid. The obtained reaction fluid was introduced into an evaporator, in which the reaction fluid was separated into a volatile phase containing the product and a nonvolatile phase containing the catalyst. The volatile phase was successively distilled for removing a low-boiling fraction, for dehydration and for removing a high-boiling fraction, thereby obtaining acetic acid. This acetic acid contained at least crotonaldehyde, ethylcrotonaldehyde and 2-methyl-2-pentenal, so that the potassium permanganate test mark of the acetic acid was as poor as 110 min.

A purification experiment was conducted for this acetic acid with the use of the same distillation column as that of Example 1 and under the same operating conditions as those of Example 1. The resultant purified acetic acid had the potassium permanganate test mark improved to at least 240 min.



Example 3

The heat balance was calculated with respect to the operation of the plant of Fig. 2.

The column A of Fig. 2, i.e., column for removing a heavy fraction from the crude acetic acid, could be operated according to the balance of Table 1. The operating pressure was 1.03 kg/cm^2 , and the column top temperature was 118°C .

Table 1

	Flow rate
line 16	34.1 kg/hr
line 17	1% of line 16
line 20	56% of line 18
line 19	line 16 - line 17

From the above, the flow rate and temperature of the overhead steam (line 18) output from the column A which can be used as a heat source for the reboiler of the column B are 76.7 kg/hr and 118°C , respectively. On the heat balance, the amount of the fluid (i.e., the overhead steam) is expressed in terms of acetic acid because the amount of the components other than acetic acid is very minute in the fluid. The latent heat of evaporation of acetic acid is 97 kcal/kg , so



that a quantity of heat of 7.4×10^3 kcal/hr can be obtained from the overhead steam output from the column A.

According to the procedures of Example 1 of the present invention; the column B of Fig. 2 can be operated in accordance with the balance specified in Table 2. The operating pressure at the column top is 400 mmHg and the column bottom temperature is 95°C.

Table 2

	flow rate
line 23	33.8 kg/hr
line 24	0.34 kg/hr
line 26	0.26 kg/hr
line 27	39 kg/hr

In this instance, the quantity of heat needed for the reboiler of the column B is 7.1×10^3 kcal/hr.

Hence,

quantity of heat carried by overhead steam from column A	>	quantity of heat needed for reboiler of column B.
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Therefore, when the column B of Fig. 1b according to the present invention is added to the purification system including the column A of Fig. 1a and when the process of Fig. 2 is employed, the column B can be



operated without the need of additional thermal energy to thereby obtain a high-quality acetic acid.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.



CLAIMS

What we claim is:

1. A method for purifying acetic acid containing at least one component selected from the group consisting of organoiodine compounds, metalloiodine compounds, iodide ions, unsaturated compounds and carbonyl compounds as an impurity, which comprises purifying the acetic acid with a distillation column having at least 30 plates by operating the distillation column under a pressure ranging from 40 to 760 mmHg at a reflux ratio of at least 4.

2. The method for purifying acetic acid as claimed in Claim 1, wherein the acetic acid to be purified is prepared by the carbonylation of methanol with the use of carbon monoxide and, methanol, a mixture of methyl acetate and water or a mixture of methyl acetate, methanol and water in a reaction medium containing a rhodium catalyst, water, acetic acid and methyl iodide.

3. The method for purifying acetic acid as claimed in Claim 2, wherein the reaction medium comprises the whole or a part of the overhead from the distillation column.

4. The method for purifying acetic acid as claimed in Claim 1, wherein purified acetic acid as a product is withdrawn outside the distillation column

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in the form of a vapor or liquid.

5. The method for purifying acetic acid as claimed in Claim 1, wherein the components as impurities are crotonaldehyde, ethylcrotonaldehyde and 2-methyl-2-pentenal.