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A METHOD OF INHIBITING POLYMERIZATION OF VINYL COMPOUND AND POLYMERIZATION INHIBITOR USED THEREIN

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a system of inhibiting polymerization of a vinyl compound. More specifically, the invention relates to a method of inhibiting polymerization of a vinyl compound, for example, acrylic acid or methacrylic acid, which is applicable to distillation for obtaining purified vinyl compound, and also relates to a polymerization inhibitor used therein.

Related State of the Art

15 Vinyl compounds such as acrylic acid and methacrylic acid are readily polymerized by application of light or heat. Especially in the process of distillation or concentration, the polymerized vinyl compounds often cause serious problems. For example, such polymerized vinyl compounds in distillation are stuck to heat transfer surface in a reboiler of a distillation column, thereby decreasing the heat transfer performance thereof. In addition, the polymer can choke the distillation column and degrade the ability thereof.

A method utilizing hydroquinone, p-methoxyphenol, or

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copper dimethyl dithiocarbamate is well known as a method of inhibiting polymerization of the vinyl compounds. Several methods have also been proposed to inhibit polymerization of vinyl compounds. These conventional methods include; one
5 utilizing at least one compound selected from the group consisting of hydroquinone, p-methoxyphenol, cresol, phenol, tert-butyl catechol, diphenylamine, phenothiazine, and methylene blue in combination with at least one compound selected from the group consisting of copper dimethyl dithiocarbamate,
10 copper diethyl dithiocarbamate, copper dibutyl dithiocarbamate, and copper salicylate (JAPANESE EXAMINED PATENT PUBLICATION No. 52-34606); one utilizing a manganese salt, such as manganese acetate, alone or in combination with hydroquinone and/or p-methoxyphenol (JAPANESE PATENT KOKAI PUBLICATION No.
15 51-98211); and one utilizing manganese dithiocarbamate or thiurams (JAPANESE PATENT KOKAI PUBLICATION No. 5-51403).

These known methods of inhibiting polymerization are, however, not applicable to distillation of vinyl compounds of relatively high concentrations under a high temperature condition.
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Acrylic acid, one of the vinyl compounds, is used as a material for water-absorbing gels and thus required to have sufficiently high purity. As a high purity acrylic acid, the total content of aldehydes, including acrolein, furfural,



benzaldehyde, and salicylaldehyde, contained in the acrylic acid is required at most several ppm.

A simple and still reliable method of aldehyde elimination is distillation of the crude or distilled acrylic acid in the presence of an aldehyde treatment agent. The aldehyde treatment agents include, for example, hydrazine hydrate, phenylhydrazine, and m-phenylenediamine. This method, however, accelerates polymerization of the vinyl compounds, especially acrylic acid.

The known polymerization inhibitors are not applicable to distillation of the vinyl compounds in the presence of the aldehyde treatment agent.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a method of inhibiting polymerization of vinyl compounds, which is applicable to distillation of the vinyl compounds of relatively high concentrations under a high temperature condition or in the presence of an aldehyde treatment agent.

Another object of the present invention is to provide a polymerization inhibitor, which is preferably applied to distillation of the vinyl compounds of relatively high concentrations under a high temperature condition or in the presence of the aldehyde treatment agent.

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These and other objects will become apparent from the following description.

The present inventors made a study on developing a novel method of inhibiting polymerization and a novel polymerization inhibitor applicable to distillation of vinyl compounds, and found that the above objects can be achieved by combining a specific metal or metal compound with a copper dithiocarbamate compound and a compound like phenothiazine, hydroquinone, or p-methoxyphenol.

The present invention provides a method of inhibiting polymerization of a vinyl compound during distillation, which comprises distilling the vinyl compound in the presence of the following components:

(1) phenothiazine, hydroquinone, p-methoxyphenol, cresol, phenol, tert-butyl catechol, diphenylamine, or methylene blue;

(2) a copper dithiocarbamate compound; and

(3) a metal, an alloy containing at least 90% by weight of the metal, an acetate of the metal, or an oxide of the metal,

wherein the metal is selected from the group consisting of chromium, magnesium, titanium, or cobalt.

The present invention also provides a polymerization inhibitor for the inhibition of polymerization during distillation of a vinyl compound, which comprises the above components (1), (2) and (3).

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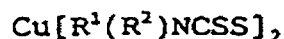


DETAILED DESCRIPTION OF THE INVENTION

The present invention is hereinafter described in detail.

Examples of the vinyl compounds in the present invention include acrylic acid, methacrylic acid, acrylic acid esters, methacrylic acid esters, acrylonitrile, and styrene. Preferred acrylic acid esters or methacrylic acid esters are C₁-C₄ alkyl esters of acrylic acid or C₁-C₄ alkyl esters of methacrylic acid.

Copper dithiocarbamate compound is, for example, represented by the general formula



in which R¹ and R² may be the same or different, and each represent alkyl, preferably of 1 to 6 carbon atoms, or R¹ and R² together represent an alkylene group, preferably of 2 to 6 carbon atoms attached to the nitrogen atom, one of the carbon atoms optionally being replaced by oxygen such as oxydiethylene group, which has the structure of $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$.

Specific examples of the copper dithiocarbamate compounds include copper dialkyl dithiocarbamates such as copper dimethyl dithiocarbamate, copper diethyl dithiocarbamate, copper dipropyl dithiocarbamate and copper dibutyl dithiocarbamate; copper cyclic alkylene dithiocarbamates such

as copper ethylene dithiocarbamate, copper trimethylene dithiocarbonate, copper tetramethylene dithiocarbamate, copper pentamethylene dithiocarbamate and copper hexamethylene dithiocarbamate; and copper cyclic oxydialkylene

5 dithiocarbamates such as copper oxydiethylene dithiocarbamate.

The content of the at least one compound selected from the group consisting of phenothiazine, hydroquinone, p-methoxyphenol, cresol, phenol, tert-butyl catechol, diphenylamine, and methylene blue depends upon the type of vinyl
10 compound to be distilled, the temperature, and the like, but is generally about 10 to 10,000 ppm by weight, preferably about 20 to 5,000 ppm by weight of the vinyl compound. The content of less than 10 ppm by weight may result in insufficient effects of polymerization inhibition. In the present
15 invention, 'at least one compound selected from the group consisting of phenothiazine, hydroquinone, p-methoxyphenol, cresol, phenol, tert-butyl catechol, diphenylamine, and methylene blue' may hereinafter be referred to simply as the 'component (1)'.

20 The content of the copper dithiocarbamate compound also depends upon the type of vinyl compound to be distilled, the temperature, and the like, but is generally about 1 to 500 ppm by weight, preferably about 5 to 100 ppm by weight of the vinyl compound. Sufficient inhibition of polymerization may



not be achieved by the content of less than 1 ppm by weight. Although the greater content of the copper dithiocarbamate compound exerts the better effects, an excessive amount of the copper dithiocarbamate compound is not preferable because of its corrosibility.

The metal which is chromium, magnesium, titanium or cobalt may be added as a elementary metal, an alloy containing the metal(at least 90% by weight), an acetate of the metal, or an oxide of the metal. In the present invention, 'a metal, an alloy containing at least 90% by weight of the metal, an acetate of the metal, or an oxide of the metal, wherein the metal is chromium, magnesium, titanium, or cobalt' may hereinafter be referred to simply as the 'metal or metal compound'. Among the metals, chromium, titanium and cobalt are preferred, and titanium is more preferred. Any alloys containing chromium, magnesium, titanium, or cobalt (at least 90% by weight) can be utilized as the alloy in the present invention. Examples of the acetate of the metal include chromium acetate, magnesium acetate, titanium acetate, and cobalt acetate whereas those of the oxide of the metal include chromium oxide, magnesium oxide, titanium oxide, and cobalt oxide. Among the metals or metal compounds, titanium metal and titanium oxide are preferred for their efficacy.

Both the copper dithiocarbamate compound and the

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component (1) may be added directly to the vinyl compound in the form of solid or powder, or alternatively their solution dissolved in an appropriate organic solvent.

5 The content of the metal or metal compound added in the form of powder or granules depends upon the type of vinyl compound to be distilled, the temperature, and the like, but is generally about 0.001 to 500 ppm by weight, preferably about 0.005 to 100 ppm by weight of the vinyl compound. The content less than 0.001 ppm by weight may result in insuffi-
10 cient inhibition of polymerization. The metal or metal compound, the copper dithiocarbamate compound and component (1) may be added to the vinyl compound separately or after being mixed together.

The powdery or granular metal or metal compound, copper
15 dithiocarbamate compound and the component (1) may be added to the vinyl compound at any timing. For example, these components may be added to a solution of vinyl compound to be distilled or to a refluxed solution in the process of distillation.

20 Although it is generally assumed that granular or powdery form is preferable for the metal or metal compound, pieces or plates of the metal or metal compound have the same effects as the powdery or granular metal or metal compound in the present invention. According to one embodiment of the



present invention, the metal or metal compound may be formed as an element of the distillation apparatus, which is contacted with the vinyl compound to be distilled. According to another embodiment of the present invention, an element of the distillation apparatus contacted with the vinyl compound to be distilled may be filled with the metal or metal compound of various shapes and forms, for example, net-shape, ring-shape, and porous bodies. Such embodiments described above are also aspects of the addition of the metal or metal compound in the present invention. To use the metal or metal compound as the element or the filler of the distillation apparatus is especially preferred in the industrial level. The surface area and the quantity of the metal or metal compound used as the element or the filler of the distillation apparatus are so determined as to preferably keep the content of the metal or metal compound in the vinyl compound to be distilled not less than 0.001 ppm by weight of the vinyl compound after consideration of the type of vinyl compound to be distilled, the temperature of distillation, and the like. Titanium metal is especially preferred for the element or the filler of the distillation apparatus.

Another polymerization inhibitor, for example, a manganese salt or thiuram, may be used together with the polymerization inhibitor of the present invention.



The conditions applied to distillation of a vinyl compound, such as the heating temperature, the pressure, and the residence time, are selected appropriately according to the type and quantity of vinyl compound to be distilled, the distillation apparatus, and the like. The distillation is carried out in the atmosphere of, for example, molecular oxygen or nitrogen.

Examples of the aldehyde treatment agents used for distillation of acrylic acid for higher purity include hydrazine compounds, such as hydrazine hydrate, phenylhydrazine, hydrazine sulfate and hydrazine hydrochloride, phenylenediamines, such as m-phenylenediamine, and their mixture of at least two kind.

The conditions applied to distillation of acrylic acid are also selected appropriately according to the distillation apparatus, the quantity of acrylic acid to be distilled, and the like, but the heating temperature of not more than 100°C is preferred.

According to the present invention, polymerization of vinyl compound during distillation can effectively be inhibited even under readily polymerizable conditions.

When a vinyl compound, especially in the case of acrylic acid, is distilled for higher purity thereof in the presence of an aldehyde treatment agent, the total amount of



polymers produced can significantly be reduced according to the present invention. For the above advantage, long time operation of the distillation, such as continuous distillation, can be carried out, and the ratio of distillate to the raw vinyl compound can be increased, thereby the raw material can effectively be utilized.

The present invention is hereinafter described in more detail by way of Examples. However, the present invention is not restricted to these Examples.

In the Examples and Comparative Examples below, ppm and % mean ppm by weight and % by weight respectively.

Examples 1 to 5

In each of examples 1 to 5, 100 ppm of p-methoxyphenol, 200 ppm of phenothiazine, and 10 to 30 ppm of copper dibutyl dithiocarbamate, and a metal or metal compound specified in Table 1 were added to 20 kg of a distilled acrylic acid solution containing 200 ppm of furfural and 100 ppm of benzaldehyde, and 0.1 percent by weight of 60% hydrazine hydrate was then added to the acrylic acid solution to make a mixture.

The mixture was subjected to vacuum distillation using a rotary evaporator under the air supply condition to get higher purity acrylic acid as a distillate, at a temperature of 83 to 85°C, at a pressure of 35 mmHg, and for 10 hours. The distillation was stopped when the concentrate in the flask reached



approximately 130 g (concentration ratio of the mixture is approximately 150), and the total amount of polymers depositing in the flask was measured. The results are shown in Table 1.

5 Table 1

Examples No.	Amount of Cu^{*1} added	Type of Metal	Amount of Metal added	Total amount of polymers produced
Example 1	10 ppm	Titanium powder	0.1 g	0.1 g
Example 2	10 ppm	Magnesium ribbon	10 ppm	1 g
Example 3	10 ppm	Magnesium Acetate powder	25 ppm	1 g
Example 4	30 ppm	Titanium Metal piece ^{*2}	2 pieces	0.01 g
Example 5	30 ppm	Titanium Oxide powder	30 ppm	0.01 g

25 *1: Copper dibutyl dithiocarbamate

*2: Each piece having a surface area of 20cm^2 was placed in gas phase and liquid phase.

Examples 6 to 8: Comparative Examples 1 and 2

30 A 300 ml flask having a packed portion of 30mm diame-

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ter(ϕ) x 300 mm height(H) (filled with metal nets of SUS316L previously washed with hot water) was used as a distillation column. An acrylic acid solution containing 100 ppm of p-methoxyphenol, 50 ppm of phenothiazine, and 10 ppm of copper dibutyl dithiocarbamate (and 10 ppm of manganese dibutyl dithiocarbamate in Comparative Example 2) was supplied to the distillation system at a rate of 150 g/hr. Acrylic acid was continuously distilled and collected from the top of the distillation column while the metal or metal compound was added to the acrylic acid solution and the air flow was supplied at a rate of 10 ml/min.. The conditions of distillation were 250 torr in pressure, the interior and column top temperature at approximately 110°C and the temperature of the bath at 120 to 130°C. The operation of the distillation was stopped after three hours, and the total amount of polymers in the packed portion and in the residual solution in the flask was measured. The results are shown in Table 2.



Table 2

	Amount of CU ^{*3} added	Type of Metal	Amount of Metal added	Total amount of polymers produced
5				
	Example 6	0	Titanium Metal piece ^{*4}	2 pieces 0.4 g
10	Example 7	0	Chromium powder	0.02 g 0.2 g
	Example 8	0	Cobalt powder	0.02 g 0.2 g
15	Compara. Exp.1	0	None	0 4 g
	Compara. Exp.2	10 ppm	None	0 4 g

*3: Manganese dibutyl dithiocarbamate

20 *4: Each piece having a surface area of 20cm² was placed in gas phase and liquid phase.

Example 9: Comparative Examples 3 and 4

25 A mixture was prepared by adding 210 ppm of hydroquinone, 1 ppm of phenothiazine, and 120 ppm of p-methoxyphenol to a solution containing 50% of methacrylic acid, 27% of methyl methacrylate, 10% of water, and 13% of a solvent. The mixture was supplied to the distillation system used in Example 6 at the rate of 150 g/hr. Methacrylic acid

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solution was continuously distilled and collected while the air flow was supplied at the rate of 10 ml/min.. The bath was heated to gradually increase the temperature from the initial value of 110°C to 135°C. After the three-hour operation at a pressure of 200 mmHg and the interior and column top temperature of approximately 120°C, the total amount of polymers found in the packed portion and in the residual solution was measured. The results are shown in Table 3.

10 Table 3

	Amount of Cu^{*1} added	Type of Metal	Amount of Metal added	Total amount of polymers produced
15	Example 9	50 ppm	Titanium Metal ^{*5} piece	2 pieces 0.001 g
20	Compara. Exp.3	0 ppm	Titanium Metal piece Titanium Metal sponge ^{*7}	1 piece 0.01 g 0.2 g
25	Compara. Exp.4	10 ppm	None	0 0.01 g

*1: Copper dibutyl dithiocarbamate

*5: Each piece having a surface area of 20cm² was placed in gas phase and liquid phase.

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*6: The piece having a surface area of 20cm² was placed in gas phase.

*7: The sponge was placed in liquid phase.

5 Examples 10 and 11: Comparative Example 5

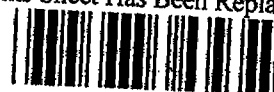
The distillation of acrylic acid containing the polymerization inhibitor described in Table 4 was carried out under the same conditions and distillation system as in Example 6. Pieces of titanium metal were used as the metal or metal compound. The results are shown in Table 4.

TABLE 4

		MP ^{*8}	PT ^{*9}	CU ^{*10}	Titanium Metal piece portion ^{*11}	Amount of polymers produced in packed Phase	Amount of polymers produced in liquid
15							
20	Example 10	200	50	10	Used	0.4 g	None
	Example 11	200	50	50	Used	0.2 g	None
25	Compara. Exp. 5	200	50.	10	Not used	3.5 g	Slightly found

*8: p-methoxyphenol

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*9: Phenothiazine

*10: Copper dibutyl dithiocarbamate

*11: Each piece having a surface area of 20cm^2 was placed in gas phase and liquid phase.

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CLAIMS

1. A method of inhibiting polymerization of a vinyl compound during distillation, which comprises distilling the vinyl compound in the presence of the following components:

(1) phenothiazine, hydroquinone, p-methoxyphenol, cresol, phenol, tert-butyl catechol, diphenylamine, or methylene blue;

(2) a copper dithiocarbamate compound; and

(3) a metal, an alloy containing at least 90% by weight of the metal, an acetate of the metal, or an oxide of the metal, wherein the metal is chromium, magnesium, titanium, or cobalt.

2. A method according to Claim 1, wherein component (3) is a powder, granules, a metal net, a block, or a moulded shape.

3. A method according to Claim 1, wherein component (3) comprises part of the distillation apparatus in contact with the vinyl compound to be distilled.

4. A method according to Claim 1, 2 or 3, wherein component (3) is titanium metal.

5. A method according to any one of Claims 1 to 4, wherein the vinyl compound comprises acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester, acrylonitrile, or styrene.

6. A method according to Claim 5, wherein the vinyl

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compound comprises acrylic acid, methacrylic acid, C₁-C₄ alkyl ester of acrylic acid, or C₁-C₄ alkyl ester of methacrylic acid.

7. A method according to any one of Claims 1 to 4,
5 wherein the vinyl compound is acrylic acid or acrylic acid ester, and distillation of acrylic acid or acrylic acid ester is carried out in the presence of an aldehyde treatment agent.

8. A method according to Claim 7, wherein the aldehyde treatment agent is a hydrazine compound.

10 9. A polymerization inhibitor for the inhibition of polymerization during distillation of a vinyl compound, which comprises:

(1) phenothiazine, hydroquinone, p-methoxyphenol, cresol, phenol, tert-butyl catechol, diphenylamine, or methylene blue;

15 (2) a copper dithiocarbamate; and

(3) a metal, an alloy containing at least 90% by weight of the metal, an acetate of the metal, or an oxide of the metal, wherein the metal is chromium, magnesium, titanium, or cobalt.

10 10. A polymerization inhibitor according to Claim 9, wherein component (3) is titanium metal.

11. A method according to Claim 1 substantially as hereinbefore described in any one of Examples 1 to 11.

12. A polymerization inhibitor according to Claim 9

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substantially as hereinbefore described in any of Examples 1
to 11.

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