

PROCESS FOR PURIFYING ACRYLIC ACID

5 The present invention relates to a process for purifying acrylic acid. More particularly, the present invention relates to a process for purifying acrylic acid obtainable by vapor phase oxidation.

Description of Related Art

10 Although a process for producing acrylic acid by vapor phase oxidation is well known as an industrial process, it is known that by-products such as aldehydes (e.g., furfural and benzaldehyde) and ketones (e.g., acetone) and the like are also produced in the process.

15 Recently, the demand for acrylic acid is increasing as a material for a water-absorbing resin that is used for, for example, paper diapers. For such application, acrylic acid having higher purity is required. Accordingly, acrylic acid is purified through distillation in the field of industry.

20 It is, however, difficult to remove the aforementioned by-products, i.e., furfural in acrylic acid produced by vapor phase oxidation through ordinary distillation. Further, when the produced acrylic acid is used as a material for an acrylic polymer without removing such impurities, various
25 problems are caused such as delay of the polymerization reaction, decrease of the degree of polymerization, and coloring



of the resultant polymer.

In order to overcome these problems, addition of a hydrazine compound in the distillation is proposed. Although the added hydrazine compound exhibits an effect to remove the impurities, this causes another problem that acrylic acid is polymerized during the distillation. The thus polymerized material in the distillation is stuck to the heat transfer surface in a reboiler of a distillation column, thereby decreasing the heat transfer performance thereof. In addition, the material can choke the distillation column and degrade the ability thereof.

Thus, a distillation method has been desired in which such polymerization is suppressed.

An object of the present invention is to provide an effective process for purifying acrylic acid produced by vapor phase oxidation while suppressing polymerization thereof.

This and other object will become apparent from the following description.

SUMMARY OF THE INVENTION

The present inventors made a study on the purification method for acrylic acid produced by vapor phase oxidation and found that the above object can be achieved by adding a hydrazine compound and a copper dithiocarbamate compound to acrylic acid produced by the vapor phase oxidation and distilling the mixture. This and further studies have led to the completion of the present invention.

The present invention relates to a process for



purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100 °C.

5 DETAILED DESCRIPTION OF THE INVENTION

The present invention is hereinafter described in detail.

Acrylic acid used in the present invention is the one obtainable by vapor oxidation of propylene and/or acrole-
10 in, that is, so-called vapor phase acrylic acid. The acrylic acid generally contains aldehydes such as furfural and benzaldehyde and ketones such as acetone by-produced in the production procedure.

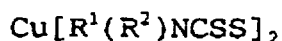
Examples of the hydrazine compounds to be used
15 include free form, hydrate or salt of hydrazine, and arylhydrazines such as phenylhydrazine, alkylhydrazine such as methylhydrazine. Hydrazine hydrate, phenylhydrazine, hydrazine sulfate and hydrazine hydrachloride are preferred. Hydrazine hydrate is more preferred.

20 The amount of the hydrazine compound to be added is usually about 50 ppm to 5000 ppm by weight, and preferably about 200 ppm to 3000 ppm by weight to the acrylic acid. By adding the hydrazine compound, the impurities, which are contained in the acrylic acid and give adverse effects when the
25 acrylic acid is used as a material for a polymer, can be removed through distillation. Especially, furfural, which is hard to be separated from acrylic acid through ordinary dis-



tillation, can be removed.

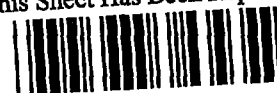
Copper dithiocarbamate compounds is, for example, represented by the general formula



5 in which R^1 and R^2 may be the same or different, and each represent alkyl, preferably of 1 to 6 carbon atoms, or R^1 and R^2 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
10 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,
15 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
20 dithiocarbamate; and copper cyclic oxydialkylene dithiocarbamates such as copper oxydiethylene dithiocarbamate.

The amount of the copper dithiocarbamate compound to be added is usually about 1 ppm to 100 ppm by weight, preferably about 5 ppm to 80 ppm by weight, and more preferably
25 about 10 ppm to 50 ppm by weight to the acrylic acid. When the added amount is too small, the effect for suppressing the polymerization is not sufficient, particularly at the initial



stage of the distillation. Excessive addition of the copper dithiocarbamate compound does not cause any specific problem in suppressing the polymerization, but is not preferable because excessive high concentration of the copper dithiocarbamate compound in a solution in the distillation vessel would tend to cause corrosion of the distillation apparatus.

Methods of adding the hydrazine compound and the copper dithiocarbamate are not limited. For example, each of them can be directly added to the acrylic acid, or they can be dissolved in the same solvent or the respective organic solvents and then can be added to the acrylic acid.

The addition temperature can be suitably decided.

The hydrazine compound and the copper dithiocarbamate compound can be added subsequently after the production of the acrylic acid, however, it is preferable that they are added just before the distillation. In the field of industry, they are usually added to the acrylic acid to be supplied to the distillation apparatus or, in some case, to a solution refluxed into the distillation vessel in the distillation.

Further, when a phenol compound is added to the acrylic acid in addition to the hydrazine compound and the copper dithiocarbamate compound, the effect of the invention is further developed.

Examples of the phenol compound include phenol, hydroquinone, methoquinone (p-methoxyphenol), catechol and



cresol.

The amount of the phenol compound to be added is usually about 10 ppm to 500 ppm by weight, and preferably about 50 ppm to 300 ppm by weight to the acrylic acid.

5 Moreover, another polymerization inhibitors such as phenothiazine and manganese salt can be further added. The phenol compound and the polymerization inhibitor can be added in the same manner as the hydrazine compound and the copper dithiocarbamate compound.

10 The thus obtained mixture of the acrylic acid containing the hydrazine compound and the copper dithiocarbamate compound is subjected to the distillation, thereby removing the impurities in the acrylic acid.

15 The distillation method is not limited, and various methods such as simple distillation and rectification can be applied. Specifically, a method used in an example disclosed in Japanese Laid-Open Patent Publication No. 49-30312 can be adopted. The distillation can be carried out in a continuous or a batchwise manner. The continuous manner is industrially
20 preferred.

In the distillation apparatus, a part contacting the liquid of the mixture or vapor of acrylic acid and the like, can be made of, for example, stainless steel such as SUS304 and SUS316.

25 The distillation temperature is not more than 100 °C, preferably not more than 80 °C, more preferably not more than 70 °C.



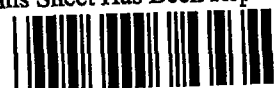
The residence time of the acrylic acid depends on the distillation temperature. When the temperature is in a range from 80 to 100 °C, the residence time is usually not more than 5 hours, preferably not more than 3 hours, more preferably not more than 1 hour. When the temperature is in a range from 70 to 80 °C, the residence time is usually not more than 20 hours, preferably not more than 10 hours, more preferably not more than 5 hour. When the temperature is not more than 70 °C, the residence time is usually not more than 30 hours, preferably not more than 20 hours, more preferably not more than 10 hour.

The concentration ratio of the solution in the distillation vessel depends upon the type of the distillation, the distillation temperature and time, the kind and the amount of the impurities, and the like.

In terms of preventing the corrosion of the distillation apparatus, the concentration of the copper dithiocarbamate is preferably maintained lower than 1 wt.%.

According to the present invention, the acrylic acid produced by vapor phase oxidation can effectively be purified while suppressing the polymerization in the distillation. As a result, it is possible to remove the impurities that are inherently contained in the acrylic acid and exhibits adverse effects when the acrylic acid is used as a material for acrylic polymer. Thus, the present invention is industrially valuable.

The present invention is hereinafter described in



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

Example 1

To 1 kg of crude acrylic acid containing 200 ppm by weight of furfural as impurity, copper dibutyl dithiocarbamate and hydrazine hydrate were added to make a mixture having copper dibutyl dithiocarbamate content of 20 ppm by weight and hydrazine hydrate of 0.1 % by weight to the crude acrylic acid.

The thus obtained mixture was subjected to vacuum distillation using an evaporator at a pressure of 50 torr and a temperature of 69 °C, and 99.5 % of the mixture was distilled for 1 hour (concentration ratio of the mixture is 200). During and after the distillation, almost no polymer was found in the residue. A content of furfural in the resultant distillate was less than 1 ppm by weight.

Examples 2 to 5

These examples were performed in the same manner as Example 1 except that the amount of copper dibutyl dithiocarbamate was changed or other additive was further added as listed in Table 1. The results are also shown in Table 1.



Table 1

Exp. No.	Content of CBD* ¹	Other Additive		Generation of Polymer in the Residue	Content of FF* ² in distillate
		Kind	Content		
2	50 ppm	None	0 ppm	Almost No Polymer	<1 ppm
3	80 ppm	None	0 ppm	Almost No Polymer	<1 ppm
4	50 ppm	MTQ* ³	100 ppm	No Polymer	<1 ppm
5	50 ppm	MTQ* ³ PTZ* ⁴	100 ppm 200 ppm	No polymer	<1 ppm

*1: CBD means copper dibutyl dithiocarbamate.

*2: FF means furfural.

*3: MTQ means methoquinone.

*4: PTZ means phenothiazine.

Comparative Examples 1 to 5

These comparative examples were also performed in the same manner as Example 1 except that other additive(s) was(were) added as listed in Table 2 instead of copper dibutyl dithiocarbamate. The results are also shown in Table 2.

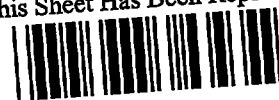


Table 2

Comparative Exp.No.	Other additive		Generation of Polymer in the Residue
	Kind	Content	
1	MTQ ^{*3}	200 ppm	Cloudiness/10 min. ^{*8} Much Polymer on the wall/End ^{*10}
2	HQ ^{*5}	200 ppm	Stains/10 min. ^{*9} Much Polymer on the wall/End ^{*10}
3	MTQ ^{*3} PTZ ^{*4}	100 ppm 200 ppm	Cloudiness/10 min. ^{*8} Stains/30 min. ^{*9} Much Polymer on the wall/End ^{*10}
4	HQ ^{*5} MA ^{*6}	200 ppm 50 ppm	Stains/10 min. ^{*9} Much Polymer on the wall/End ^{*10}
5	MTQ ^{*3} MBD ^{*7} PTZ ^{*4}	100 ppm 50 ppm 200 ppm	Cloudiness/10 min. ^{*8} Stains/30 min. ^{*9} Much Polymer on the wall/End ^{*10}

*3 and *4: MTQ and PTZ have the same meanings as in Table 1.

*5: HQ means hydroquinone.

*6: MA means manganese acetate.

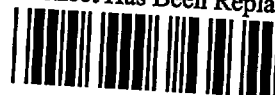
*7: MBD means manganese dibutyl dithiocarbamate.



*8: Cloudiness of the mixture was found due to the polymer generation about indicated minutes after starting the distillaion.

5 *9: Stains on the inner wall of the distillation vessel was found due to the polymer generation indicated minutes after starting the distillation.

*10: Large amount of the polymer stuck to the wall of the distillation vessel was found after the distillation.

Claims

1. A process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper
5 dithiocarbamate compound at a temperature of not more than 100 °C.

2. A process according to Claim 1, wherein the mixture also comprises a phenol compound.

3. A process according to Claim 2, wherein the
10 phenol compound is phenol, hydroquinone, methoquinone, catechol or cresol.

4. A process according to Claim 1, 2 or 3, wherein the copper dithiocarbamate compound is a copper dialkyl dithiocarbamate.

5. A process according to any one of the preceding
15 Claims, wherein the copper dithiocarbamate compound is a copper di-loweralkyl dithiocarbamate.

6. A process according to Claim 1, 2 or 3, wherein the copper dithiocarbamate compound is copper dimethyl
20 dithiocarbamate, copper diethyl dithiocarbamate, copper dipropyl dithiocarbamate, copper dibutyl dithiocarbamate, copper ethylene dithiocarbamate, copper trimethylene dithiocarbamate, copper tetramethylene dithiocarbamate, copper pentamethylene dithiocarbamate, copper hexamethylene
25 dithiocarbamate or copper oxydiethylene dithiocarbamate.

7. A process according to any one of preceding Claims, wherein the hydrazine compound is hydrazine hydrate,





phenylhydrazine, hydrazine sulfate or hydrazine hydrochloride.

8. A process according to any one of the preceding Claims, wherein the temperature in the distillation is not more than 80 °C.

5 9. A process according to any one of the preceding Claims, wherein the temperature in the distillation is not more than 70 °C.

10. A process according to Claim 1 substantially as hereinbefore described in any one of Examples 1 to 5.



A B S T R A C T

PROCESS FOR PURIFYING ACRYLIC ACID

The present invention provides a process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100 °C.

According to the present invention, the acrylic acid produced by vapor phase oxidation can effectively be purified while suppressing the polymerization in the distillation.

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PROCESS FOR PURIFYING ACRYLIC ACID

The present invention relates to a process for purifying acrylic acid. More particularly, the present invention relates to a process for purifying acrylic acid obtainable by vapor phase oxidation.

DESCRIPTION OF RELATED ART

Although a process for producing acrylic acid by vapor phase oxidation is well known as an industrial process, it is known that by-products such as aldehydes (e.g., furfural and benzaldehyde) and ketones (e.g., acetone) and the like are also produced in the process.

Recently, the demand for acrylic acid is increasing as a material for a water-absorbing resin that is used for, for example, paper diapers. For such application, acrylic acid having higher purity is required. Accordingly, acrylic acid is purified through distillation in the field of industry.

It is, however, difficult to remove the aforementioned by-products, i.e., furfural in acrylic acid produced by vapor phase oxidation through ordinary distillation. Further, when the produced acrylic acid is used as a material for an acrylic polymer without removing such impurities, various problems are caused such as delay of the polymerization reaction, decrease of the degree of polymerization, and coloring of the resultant polymer.

In order to overcome these problems, addition of a hydrazine compound in the distillation is proposed. Although the added hydrazine compound exhibits an effect to remove the impurities, this causes another problem that acrylic acid is polymerized during the distillation. The thus polymerized

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material in the distillation is stuck to the heat transfer surface in a reboiler of a distillation column, thereby decreasing the heat transfer performance thereof. In addition, the material can choke the distillation column and degrade the ability thereof.

Thus, a distillation method has been desired in which such polymerization is suppressed.

An object of the present invention is to provide an effective process for purifying acrylic acid produced by vapor phase oxidation while suppressing polymerization thereof.

This and other object will become apparent from the following description.

SUMMARY OF THE INVENTION

The present inventors made a study on the purification method for acrylic acid produced by vapor phase oxidation and found that the above object can be achieved by adding a hydrazine compound and a copper dithiocarbamate compound to acrylic acid produced by the vapor phase oxidation and distilling the mixture. This and further studies have led to the completion of the present invention.

The present invention relates to a process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100°C.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention is hereinafter described in detail.

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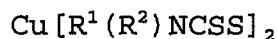
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Acrylic acid used in the present invention is the one obtainable by vapor oxidation of propylene and/or acrolein, that is, so-called vapor phase acrylic acid. The acrylic acid generally contains aldehydes such as furfural and benzaldehyde and ketones such as acetone by-produced in the production procedure.

Examples of the hydrazine compounds to be used include free form, hydrate or salt of hydrazine, and arylhydrazines such as phenylhydrazine, alkylhydrazine such as methylhydrazine. Hydrazine hydrate, phenylhydrazine, hydrazine sulfate and hydrazine hydrachloride are preferred. Hydrazine hydrate is more preferred.

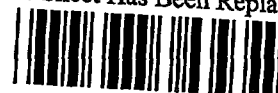
The amount of the hydrazine compound to be added is usually about 50 ppm to 5000 ppm by weight, and preferably about 200 ppm to 3000 ppm by weight to the acrylic acid. By adding the hydrazine compound, the impurities, which are contained in the acrylic acid and give adverse effects when the acrylic acid is used as a material for a polymer, can be removed through distillation. Especially, furfural, which is hard to be separated from acrylic acid through ordinary distillation, can be removed.

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



in which R^1 and R^2 may be the same or different, and each represent alkyl, preferably of 1 to 6 carbon atoms, or R^1 and R^2 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 $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$.

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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 dithiocarbamates such as copper oxydiethylene dithiocarbamate. The copper dithiocarbamate may be a copper di(C₁₋₆)alkyl dithiocarbamate.

The amount of the copper dithiocarbamate compound to be added is usually about 1 ppm to 100 ppm by weight, preferably about 5 ppm to 80 ppm by weight, and more preferably about 10 ppm to 50 ppm by weight to the acrylic acid. When the added amount is too small, the effect for suppressing the polymerization is not sufficient, particularly at the initial stage of the distillation. Excessive addition of the copper dithiocarbamate compound does not cause any specific problem in suppressing the polymerization, but is not preferable because excessive high concentration of the copper dithiocarbamate compound in a solution in the distillation vessel would tend to cause corrosion of the distillation apparatus.

Methods of adding the hydrazine compound and the copper dithiocarbamate are not limited. For example, each of them can be directly added to the acrylic acid, or they can be dissolved in the same solvent or the respective organic solvents and then can be added to the acrylic acid.

The addition temperature can be suitably decided.

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The hydrazine compound and the copper dithiocarbamate compound can be added subsequently after the production of the acrylic acid, however, it is preferable that they are added just before the distillation. In the field of industry, they are usually added to the acrylic acid to be supplied to the distillation apparatus or, in some case, to a solution refluxed into the distillation vessel in the distillation.

Further, when a phenol compound is added to the acrylic acid in addition to the hydrazine compound and the copper dithiocarbamate compound, the effect of the invention is further developed.

Examples of the phenol compound include phenol, hydroquinone, methoquinone (p-methoxyphenol), catechol and cresol.

The amount of the phenol compound to be added is usually about 10 ppm to 500 ppm by weight, and preferably about 50 ppm to 300 ppm by weight to the acrylic acid.

Moreover, another polymerization inhibitors such as phenothiazine and manganese salt can be further added. The phenol compound and the polymerization inhibitor can be added in the same manner as the hydrazine compound and the copper dithiocarbamate compound.

The thus obtained mixture of the acrylic acid containing the hydrazine compound and the copper dithiocarbamate compound is subjected to the distillation, thereby removing the impurities in the acrylic acid.

The distillation method is not limited, and various methods such as simple distillation and rectification can be applied. Specifically, a method used in an example disclosed

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in Japanese Laid-Open Patent Publication No. 49-30312 can be adopted. The distillation can be carried out in a continuous or a batchwise manner. The continuous manner is industrially preferred.

In the distillation apparatus, a part contacting the liquid of the mixture or vapor of acrylic acid and the like, can be made of, for example, stainless steel such as SUS304 and SUS316.

The distillation temperature is not more than 100°C, preferably not more than 80°C, more preferably not more than 70°C.

The residence time of the acrylic acid depends on the distillation temperature. When the temperature is in a range from 80 to 100°C, the residence time is usually not more than 5 hours, preferably not more than 3 hours, more preferably not more than 1 hour. When the temperature is in a range from 70 to 80°C, the residence time is usually not more than 20 hours, preferably not more than 10 hours, more preferably not more than 5 hours. When the temperature is not more than 70°C, the residence time is usually not more than 30 hours, preferably not more than 20 hours, more preferably not more than 10 hour.

The concentration ratio of the solution in the distillation vessel depends upon the type of the distillation, the distillation temperature and time, the kind and the amount of the impurities, and the like.

In terms of preventing the corrosion of the distillation apparatus, the concentration of the copper dithiocarbamate is preferably maintained lower than 1 wt.%.

According to the present invention, the acrylic acid

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produced by vapor phase oxidation can effectively be purified while suppressing the polymerization in the distillation. As a result, it is possible to remove the impurities that are inherently contained in the acrylic acid and exhibits adverse effects when the acrylic acid is used as a material for acrylic polymer. Thus, the present invention is industrially valuable.

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

Example 1

To 1 kg of crude acrylic acid containing 200 ppm by weight of furfural as impurity, copper dibutyl dithiocarbamate and hydrazine hydrate were added to make a mixture having copper dibutyl dithiocarbamate content of 20 ppm by weight and hydrazine hydrate of 0.1% by weight to the crude acrylic acid.

The thus obtained mixture was subjected to vacuum distillation using an evaporator at a pressure of 65789 pascal (50 torr) and a temperature of 69°C, and 99.5% of the mixture was distilled for 1 hour (concentration ratio of the mixture is 200). During and after the distillation, almost no polymer was found in the residue. A content of furfural in the resultant distillate was less than 1 ppm by weight.

Examples 2 to 5.

These examples were performed in the same manner as Example 1 except that the amount of copper dibutyl dithiocarbamate was changed or other additive was further added as listed in Table 1. The results are also shown in Table 1.

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Table 1

Exp. No.	Content of CBD* ¹	Other Additive		Generation of Polymer in the Residue	Content of FF* ² in distillate
		Kind	Content		
2	50 ppm	None	0 ppm	Almost No Polymer	< 1 ppm
3	80 ppm	None	0 ppm	Almost No Polymer	< 1 ppm
4	50 ppm	MTQ* ³	100 ppm	No Polymer	< 1 ppm
5	50 ppm	MTQ* ³ PTZ* ⁴	100 ppm 200 ppm	No Polymer	< 1 ppm

*1: CBD means copper dibutyl dithiocarbamate.

*2: FF means furfural.

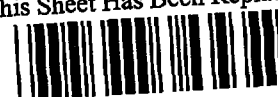
*3: MTQ means methoquinone.

*4: PTZ means phenothiazine.

Comparative Examples 1 to 5

These comparative examples were also performed in the same manner as Example 1 except that other additive(s) was(were) added as listed in Table 2 instead of copper dibutyl dithiocarbamate. The results are also shown in Table 2.

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Table 2

Comparative Exp. No.	Other additive		Generation of Polymer in the Residue
	Kind	Content	
1	MTQ ^{*3}	200 ppm	Cloudiness/10 min. ^{*8} Much Polymer on the wall/End ^{*10}
2	HQ ^{*5}	200 ppm	Stains/10 min. ^{*9} Much Polymer on the wall/End ^{*10}
3	MTQ ^{*3}	100 ppm	Cloudiness/10 min. ^{*8}
	PTZ ^{*4}	200 ppm	Stains/30 min. ^{*9} Much Polymer on the wall/End ^{*10}
4	HQ ^{*5}	200 ppm	Stains/10 min. ^{*9}
	MA ^{*6}	50 ppm	Much Polymer on the wall/End ^{*10}
5	MTQ ^{*3}	100 ppm	Cloudiness/10 min. ^{*8}
	MBD ^{*7}	50 ppm	Stains/30 min. ^{*9}
	PTZ ^{*4}	200 ppm	Much Polymer on the wall/End ^{*10}

*3 and *4: MTQ and PTZ have the same meanings as in Table 1.

*5: HQ means hydroquinone.

*6: MA means manganese acetate.

*7: MBD means manganese dibutyl dithiocarbamate.

*8: Cloudiness of the mixture was found due to the polymer generation about indicated minutes after starting the distillation.

*9: Stains on the inner wall of the distillation vessel was found due to the polymer generation indicated minutes after starting the distillation.

*10: Large amount of the polymer stuck to the wall of the distillation vessel was found after the distillation.

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CLAIMS

1. A process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100°C.
2. A process according to Claim 1, wherein the mixture also comprises a phenol compound.
3. A process according to Claim 2, wherein the phenol compound is phenol, hydroquinone, methoquinone, catechol or cresol.
4. A process according to Claim 1, 2, or 3, wherein the copper dithiocarbamate compound is a copper dialkyl dithiocarbamate.
5. A process according to any one of the preceding Claims, wherein the copper dithiocarbamate compound is a copper di-(C₁₋₆)alkyl dithiocarbamate.
6. A process according to Claim 1, 2, or 3, wherein the copper dithiocarbamate compound is copper dimethyl dithiocarbamate, copper diethyl dithiocarbamate, copper dipropyl dithiocarbamate, copper dibutyl dithiocarbamate, copper ethylene dithiocarbamate, copper trimethylene dithiocarbamate, copper tetramethylene dithiocarbamate, copper pentamethylene dithiocarbamate, copper hexamethylene dithiocarbamate or copper oxydiethylene dithiocarbamate.
7. A process according to any one of preceding Claims, wherein the hydrazine compound is hydrazine hydrate, phenylhydrazine, hydrazine sulfate or hydrazine hydrochloride.

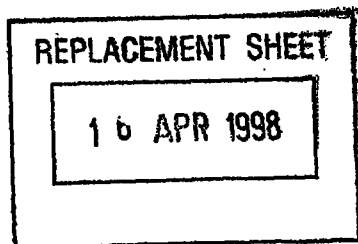
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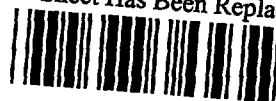
8. A process according to any one of the preceding Claims, wherein the temperature in the distillation is not more than 80°C.

9. A process according to any one of the preceding Claims, wherein the temperature in the distillation is not more than 70°C.

10. A process according to Claim 1 substantially as hereinbefore described in any one of Examples 1 to 5.



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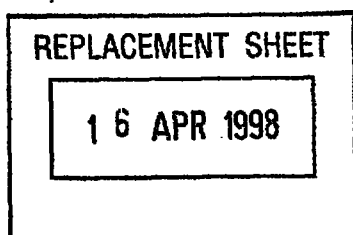


PROCESS FOR PURIFYING ACRYLIC ACID

ABSTRACT

The present invention provides a process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100°C.

According to the present invention, the acrylic acid produced by vapor phase oxidation can effectively be purified while suppressing the polymerization in the distillation.



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REPLACEMENT SHEET

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PROCESS FOR PURIFYING ACRYLIC ACID

The present invention relates to a process for purifying acrylic acid. More particularly, the present invention relates to a process for purifying acrylic acid obtainable by vapor phase oxidation.

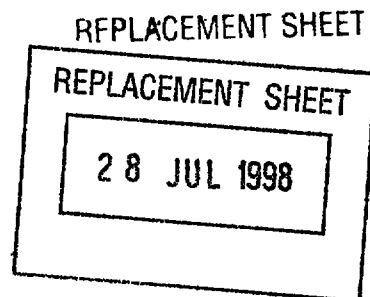
DESCRIPTION OF THE RELATED ART

Although a process for producing acrylic acid by vapor phase oxidation is well known as an industrial process, it is known that by-products such as aldehydes (e.g., furfural and benzaldehyde) and ketones (e.g., acetone) and the like are also produced in the process.

Recently, the demand for acrylic acid is increasing as a material for a water-absorbing resin that is used for, for example, paper diapers. For such application, acrylic acid having higher purity is required. Accordingly, acrylic acid is purified through distillation in the field of industry.

It is, however, difficult to remove the aforementioned by-products, i.e., furfural in acrylic acid produced by vapor phase oxidation through ordinary distillation. Further, when the produced acrylic acid is used as a material for an acrylic polymer without removing such impurities, various problems are caused such as delay of the polymerization reaction, decrease of the degree of polymerization, and coloring of the resultant polymer.

In order to overcome these problems, addition of a hydrazine compound in the distillation is proposed. Although the added hydrazine compound exhibits an effect to remove the impurities, this causes another problem that acrylic acid is polymerized during the distillation. The thus polymerized



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material in the distillation is stuck to the heat transfer surface in a reboiler of a distillation column, thereby decreasing the heat transfer performance thereof. In addition, the material can choke the distillation column and degrade the ability thereof.

Thus, a distillation method has been desired in which such polymerization is suppressed.

An object of the present invention is to provide an effective process for purifying acrylic acid produced by vapor phase oxidation while suppressing polymerization thereof.

This and other object will become apparent from the following description.

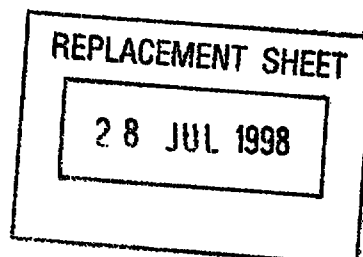
SUMMARY OF THE INVENTION

The present invention made a study on the purification method for acrylic acid produced by vapor phase oxidation and found that the above object can be achieved by adding a hydrazine compound and a copper dithiocarbamate compound to acrylic acid produced by the vapor phase oxidation and distilling the mixture. This and further studies have led to the completion of the present invention.

The present invention relates to a process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100°C.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is hereinafter described in detail.

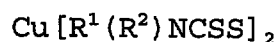


Acrylic acid used in the present invention is the one obtainable by vapor oxidation of propylene and/or acrolein, that is, so-called vapor phase acrylic acid. The acrylic acid generally contains aldehydes such as furfural and benzaldehyde and ketones such as acetone by-produced in the production procedure.

Examples of the hydrazine compounds to be used include free form, hydrate or salt of hydrazine, and arylhydrazines such as phenylhydrazine, alkylhydrazine such as methylhydrazine. Hydrazine hydrate, phenylhydrazine, hydrazine sulfate and hydrazine hydrachloride are preferred. Hydrazine hydrate is more preferred.

The amount of the hydrazine compound to be added is usually about 50 ppm to 5000 ppm by weight, and preferably about 200 ppm to 3000 ppm by weight to the acrylic acid. By adding the hydrazine compound, the impurities, which are contained in the acrylic acid and give adverse effects when the acrylic acid is used as a material for a polymer, can be removed through distillation. Especially, furfural, which is hard to be separated from acrylic acid through ordinary distillation, can be removed.

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



in which R^1 and R^2 may be the same or different, and each represent alkyl, preferably of 1 to 6 carbon atoms, or R^1 and R^2 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 $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$.

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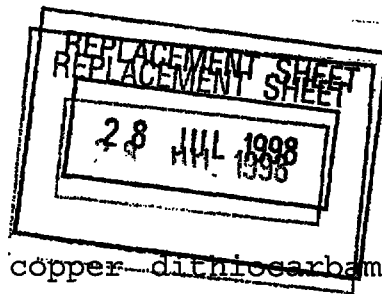
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Specific examples of the copper dithiocarbamate compounds include copper dialkyl dithiocarbamates such as copper dimethyl dithiocarbamate, copper diethyl dithiocarbamate, copper dipropyl dithiocarbamate and copper dibutyl dithiocarbamate; copper cyclic alkylene dithiocarbamates such as copper ethylene dithiocarbamate, copper trimethylene dithiocarbonate, copper tetramethylene dithiocarbamate, copper pentamethylene dithiocarbamate and copper hexamethylene dithiocarbamate; and copper cyclic oxydialkylene dithiocarbamates such as copper oxydiethylene dithiocarbamate. The copper dithiocarbamate may be a copper di(C₁₋₆)alkyl dithiocarbamate.

The amount of the copper dithiocarbamate compound to be added is usually about 1 ppm to 100 ppm by weight, preferably about 5 ppm to 80 ppm by weight, and more preferably about 10 ppm to 50 ppm by weight to the acrylic acid. When the added amount is too small, the effect for suppressing the polymerization is not sufficient, particularly at the initial stage of the distillation. Excessive addition of the copper dithiocarbamate compound does not cause any specific problem in suppressing the polymerization, but is not preferable because excessive high concentration of the copper dithiocarbamate compound in a solution in the distillation vessel would tend to cause corrosion of the distillation apparatus.

Methods of adding the hydrazine compound and the copper dithiocarbamate are not limited. For example, each of them can be directly added to the acrylic acid, or they can be dissolved in the same solvent or the respective organic solvents and then can be added to the acrylic acid.

The addition temperature can be suitably decided.



The hydrazine compound and the copper dithiocarbamate compound can be added subsequently after the production of the acrylic acid, however, it is preferable that they are added just before the distillation. In the field of industry, they are usually added to the acrylic acid to be supplied to the distillation apparatus or, in some case, to a solution refluxed into the distillation vessel in the distillation.

Further, when a phenol compound is added to the acrylic acid in addition to the hydrazine compound and the copper dithiocarbamate compound, the effect of the invention is further developed.

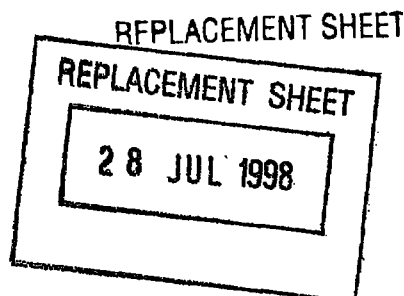
Examples of the phenol compound include phenol, hydroquinone, methoquinone (p-methoxyphenol), catechol and cresol.

The amount of the phenol compound to be added is usually about 10 ppm to 500 pm by weight, and preferably about 50 ppm to 300 ppm by weight to the acrylic acid.

Moreover, another polymerization inhibitors such as phenothiazine and manganese salt can be further added. The phenol compound and the polymerization inhibitor can be added in the same manner as the hydrazine compound and the copper dithiocarbamate compound.

The thus obtained mixture of the acrylic acid containing the hydrazine compound and the copper dithiocarbamate compound is subjected to the distillation, thereby removing the impurities in the acrylic acid.

The distillation method is not limited, and various methods such as simple distillation and rectification can be applied. Specifically, a method used in an example disclosed



in Japanese Laid-Open Patent Publication No. 49-30312 can be adopted. The distillation can be carried out in a continuous or a batchwise manner. The continuous manner is industrially preferred.

In the distillation apparatus, a part contacting the liquid of the mixture or vapor of acrylic acid and the like, can be made of, for example, stainless steel such as SUS304 and SUS316.

The distillation temperature is not more than 100°C, preferably not more than 80°C, more preferably not more than 70°C.

The residence time of the acrylic acid depends on the distillation temperature. When the temperature is in a range from 80 to 100°C, the residence time is usually not more than 5 hours, preferably not more than 3 hours, more preferably not more than 1 hour. When the temperature is in a range from 70 to 80°C, the residence time is usually not more than 20 hours, preferably not more than 10 hours, more preferably not more than 5 hours. When the temperature is not more than 70°C, the residence time is usually not more than 30 hours, preferably not more than 20 hours, more preferably not more than 10 hour.

The concentration ratio of the solution in the distillation vessel depends upon the type of the distillation, the distillation temperature and time, the kind and the amount of the impurities, and the like.

In terms of preventing the corrosion of the distillation apparatus, the concentration of the copper dithiocarbamate is preferably maintained lower than 1 wt.%.

According to the present invention, the acrylic acid

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produced by vapor phase oxidation can effectively be purified while suppressing the polymerization in the distillation. As a result, it is possible to remove the impurities that are inherently contained in the acrylic acid and exhibits adverse effects when the acrylic acid is used as a material for acrylic polymer. Thus, the present invention is industrially valuable.

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

Example 1

To 1 kg of crude acrylic acid containing 200 ppm by weight of furfural as impurity, copper dibutyl dithiocarbamate and hydrazine hydrate were added to make a mixture having copper dibutyl dithiocarbamate content of 200 ppm by weight and hydrazine hydrate of 0.1% by weight to the crude acrylic acid.

The thus obtained mixture was subjected to vacuum distillation using an evaporator at a pressure of 65789 pascal (50 torr) and a temperature of 69°C, and 99.5% of the mixture was distilled for 1 hour (concentration ratio of the mixture is 200). During and after the distillation, almost no polymer was found in the residue. A content of furfural in the resultant distillate was less than 1 ppm by weight.

Examples 2 to 5.

These examples were performed in the same manner as Example 1 except that the amount of copper dibutyl dithiocarbamate was changed or other additive was further added as listed in Table 1. The results are also shown in Table 1.

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Table 1

Exp. No.	Content of CBD* ¹	Other Additive		Generation of Polymer in the the Residue	Content of FF* ² in distillate
		Kind	Content		
2	50 ppm	None	0 ppm	Almost No Polymer	< 1 ppm
3	80 ppm	None	0 ppm	Almost No Polymer	< 1 ppm
4	50 ppm	MTQ* ³	100 ppm	No Polymer	< 1 ppm
5	50 ppm	MTQ* ³ PTZ* ⁴	100 ppm 200 ppm	No Polymer	< 1 ppm

*1: CBD means copper dibutyl dithiocarbamate.

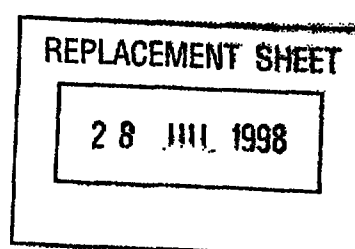
*2: FF means furfural.

*3: MTQ means methoquinone.

*4: PTZ means phenothiazine.

Comparative Examples 1 to 5

These comparative examples were also performed in the same manner as Example 1 except that other additive(s) was(were) added as listed in Table 2 instead of copper dibutyl dithiocarbamate. The results are also shown in Table 2.



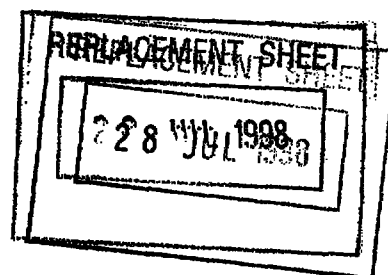


Table 2

Comparative Exp. No.	Other additive		Generation of Polymer in the Residue
	Kind	Content	
1	MTQ ^{*3}	200 ppm	Cloudiness/10 min. ^{*8} Much Polymer on the wall/End ^{*10}
2	HQ ^{*5}	200 ppm	Stains/10 min. ^{*9} Much Polymer on the wall/End ^{*10}
3	MTQ ^{*3} PTZ ^{*4}	100 ppm 200 ppm	Cloudiness/10 min. ^{*8} Stains/30 min. ^{*9} Much Polymer on the wall/End ^{*10}
4	HQ ^{*5} MA ^{*6}	200 ppm 50 ppm	Stains/10 min. ^{*9} Much Polymer on the wall/End ^{*10}
5	MTQ ^{*3} MBD ^{*7} PTZ ^{*4}	100 ppm 50 ppm 200 ppm	Cloudiness/10 min. ^{*8} Stains/30 min. ^{*9} Much Polymer on the wall/End ^{*10}

*3 and *4: MTQ and PTZ have the same meanings as in Table 1.

*5: HQ means hydroquinone.

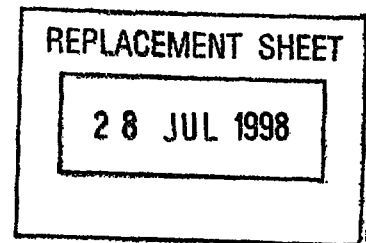
*6: MA means manganese acetate.

*7: MBD means manganese dibutyl dithiocarbamate.

*8: Cloudiness of the mixture was found due to the polymer generation about indicated minutes after starting the distillation.

*9: Stains on the inner wall of the distillation vessel was found due to the polymer generation indicated minutes after starting the distillation.

*10: Large amount of the polymer stuck to the wall of the distillation vessel was found after the distillation.

**CLAIMS**

1. A process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic cid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100°C.
2. A process according to Claim 1, wherein the mixture also comprises a phenol compound.
3. A process according to Claim 2, wherein the phenol compound is phenol, hydroquinone, methoquinone, catechol or cresol.
4. A process according to Claims 1, 2, or 3, wherein the copper dithiocarbamate compound is a copper dialkyl dithiocarbamate.
5. A process according to any one of the preceding Claims, wherein the copper dithiocarbamate compound is a copper di-(C₁₋₆)alkyl dithiocarbamate.
6. A process according to Claims 1, 2, or 3, wherein the copper dithiocarbamate compound is copper dimethyl dithiocarbamate, copper diethyl dithiocarbamate, copper dipropyl dithiocarbamate, copper dibutyl dithiocarbamate, copper ethylene dithiocarbamate, copper trimethylene dithiocarbamate, copper tetramethylene dithiocarbamate, copper pentamethylene dithiocarbamate, copper hexamethylene dithiocarbamate or copper oxydiethylene dithiocarbamate.
7. A process according to any one of preceding Claims, wherein the hydrazine compound is hydrazine hydrate, phenylhydrazine, hydrazine sulfate or hydrazine hydrochloride.

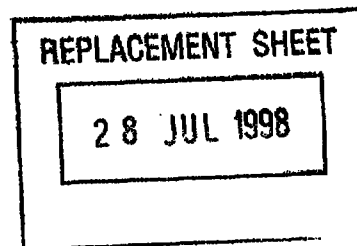


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8. A process according to any one of the preceding Claims, wherein the temperature in the distillation is not more than 80°C.

9. A process according to any one of the preceding Claims, wherein the temperature in the distillation is not more than 70°C.

10. A process according to Claim 1 substantially as hereinbefore described in any one of Examples 1 to 5.



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PROCESS FOR PURIFYING ACRYLIC ACID

ABSTRACT

The present invention provides a process for purifying acrylic acid obtainable by vapor phase oxidation which comprises distilling a mixture comprising acrylic acid, a hydrazine compound and a copper dithiocarbamate compound at a temperature of not more than 100°C.

According to the present invention, the acrylic acid produced by vapor phase oxidation can effectively be purified while suppressing the polymerization in the distillation.

