

PRODUCTION OF ACRYLIC ACID AND INHIBITION OF
POLYMERIZATION THEREOF

Field of the Invention

5 The present invention relates to a method for producing acrylic acid in which propylene and/or acrolein is catalytically oxidized in gas phase and a method for inhibiting polymerization of acrylic acid.

10 Background of the Invention

 Currently, acrylic acid is industrially produced by a method in which propylene and/or acrolein is catalytically oxidized in gas phase by using a molecular oxygen-containing gas. For purifying the resulting acrylic acid, there are
15 widely used methods in which an oxidation reaction product gas containing acrylic acid is cooled and/or absorbed by water to obtain an aqueous acrylic acid solution, thereafter, first, acrylic acid is extracted using an extraction agent or an acrylic acid is dehydrated by distillation using an
20 azeotropic agent which boils with water for separation to obtain a crude acrylic acid, then, fractions having low boiling point are separated by distillation and fractions having high boiling point are separated by distillation and, finally, the purified acrylic acid is obtained.

25 However, it is known that acrylic acid has such

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property that it causes polymerization thereof easily and intensively by heat, light, peroxide and the like. Therefore, when acrylic acid is purified by distillation, an ability of a distillation column decreases due to generation of a large
5 amount of the polymer(s) and heat transferring ability of a reboiler of a distillation column decreases due to adhesion of the polymer(s) on a heat transferring surface of the reboiler, and in addition, clogging occurs in the distillation column by the polymer(s). These phenomena are
10 extremely large obstructions in a process for producing acrylic acid, and it is extremely important to suppress the polymerization in the point of industrialization.

Therefore, for inhibiting the polymerization of acrylic acid during purification thereof, a lot of methods
15 have been conventionally suggested and conducted in which so-called polymerization inhibitors are used. Typical examples of the polymerization inhibitor include phenols such as hydroquinone, p-methoxyphenol and 2,6-di-t-butylphenol, dibenzo-p-thiazines such as phenothiazine and methylene blue,
20 copper salts such as copper dibutyldithiocarbamates, nitro compounds, nitroso compounds, N-oxyl compounds and the like. For example, Japanese Patent Application Publication (JP-B) No. 49-3514 discloses copper dibutyl dithiocarbamate is used as a polymerization inhibitor in distillation and
25 concentration step in production of unsaturated carboxylic

acids or esters thereof. In distillation of an acrylic acid, the above-described polymerization inhibitors are generally used in combination of two or more, or together with a molecular oxygen-containing gas if necessary. For example, 5 there are known combinations of at least one moiety selected from hydroquinone, hydroquinone monomethyl ether, phenothiazine and the like, a copper salt such as copper dimethyl dithiocarbamate and the like, and molecular oxygen (Japanese Patent Application Laid-open (JP-A) No. 49-85016), 10 combinations of phenols, manganese salts and hindered phenols (JP-A No. 5-140027), combinations of a N-oxy compound with at least one compound of phenothiazine, aromatic amines and phenols (JP-A No. 5-320217), and the like.

However, polymerization in purification of acrylic 15 acid is significantly influenced by purification processes, distillation temperature, residence time and the like, and the above conventional methods are not satisfactory for improving purification ability. Therefore, more efficient methods for inhibiting the polymerization are currently 20 required.

Objects of the present invention are to provide a method for producing acrylic acid, a polymerization inhibiting method and a purifying method which are more efficient mainly in purifying by distillation of acrylic acid, 25 especially in purifying acrylic acid by distillation from an

aqueous crude solution obtained by catalytic oxidation in a gas phase of propylene and/or acrolein. In particular, the object is to provide a polymerization inhibiting method in a process adopting not extraction but azeotropic dehydration
5 for removing water.

In a method for producing acrylic acid in which an aqueous acrylic acid solution obtained by catalytic oxidation in a gas phase of propylene and/or acrolein by a molecular oxygen-containing gas is dehydrated by distillation using an
10 azeotropic agent and then purification of acrylic acid is conducted by separating fractions having low boiling points by distillation and separating fractions having high boiling points by distillation, the degree of polymerization of acrylic acid is higher as compared with that in a method for
15 producing acrylic acid in which acrylic acid is extracted from the aqueous solution thereof using an extraction agent and then purification is conducted by separating fractions having low boiling points by distillation and separating fractions having high boiling points by distillation, and even if
20 conventionally known polymerization inhibitors such as phenothiazine, copper dibutyl dithiocarbamate, hydroquinone, p-methoxyphenol and the like are used alone or in combination, a satisfactory polymerization inhibiting effect in former method using an azeotropic agent can not be expected as
25 compared with that in a latter method in which a purification

process of an aqueous acrylic acid solution is conducted by using an extraction agent.

SUMMARY OF THE INVENTION

5 The present inventors have intensively studied to find a method providing an excellent an polymerization inhibiting effect even in a purification process of acrylic acid containing a step in which dehydration is conducted by distillation using an azeotropic agent. As a result, the
10 present inventors have found that acrylic acid can be purified at approximately the same degree of polymerization inhibiting effect as in a process adopting an extraction step using an extraction agent in the presence of a known polymerization inhibitor such as described above, even in a process
15 comprising an azeotropic dehydration step, when a specific substance is allowed to exist in an aqueous acrylic acid solution in a process of the dehydration, and have thus completed the present invention.

 Accordingly, the present invention provides a method
20 for producing acrylic acid comprising a step of catalytically oxidizing propylene and/or acrolein in gas phase by using a molecular oxygen-containing gas to obtain an aqueous crude acrylic acid solution, and a step of dehydrating the solution by distillation in the presence of
25 (i) at least one moiety selected from ammonia, ammonium salts,

aliphatic primary monoamines, aliphatic primary diamines, aliphatic primary polyamines, aromatic primary amines, amino acids and alkanolamines and (ii) at least one moiety selected from dibenzo-p-thiazines and copper dithiocarbamates.

5 Further, the present invention provides a method for inhibiting the polymerization of acrylic acid in which (i) at least one moiety selected from ammonia, ammonium salts, aliphatic primary monoamines, aliphatic primary diamines, aliphatic primary polyamines, aromatic primary amines, amino
10 acids and alkanolamines and (ii) at least one moiety selected from dibenzo-p-thiazines and copper dithiocarbamates are allowed to exist in a crude acrylic acid or an aqueous solution thereof, and also provides a method for purifying acrylic acid in which distillation is conducted in the presence of the
15 above-described (i) and (ii) substances.

Detailed Description of the Invention

The present invention mainly relates to a method in which propylene and/or acrolein is catalytically oxidized in
20 a gas phase using a molecular oxygen-containing gas to obtain an aqueous crude acrylic acid solution and in which the resulting aqueous crude acrylic acid solution is dehydrated by distillation. The aqueous crude acrylic acid solution can be obtained by cooling and/or absorption into water of a gas
25 containing crude acrylic acid. The gas can be obtained by

a one-step oxidation method of propylene, by a two-step oxidation method of propylene via acrolein, by a method in which a part of an exhaust gas from an acrylic acid absorption column is recycled to an oxidation reaction or by a method
5 in which this exhaust gas is made harmless and recycled by passing through an exhaust gas burning apparatus.

In the present invention, an azeotropic agent which boils with water is generally used in dehydration by distillation of an aqueous crude acrylic acid solution.

10 The main composition of the aqueous crude acrylic acid solution differs depending on a catalyst used in a gas-phase catalytic oxidation and the reaction conditions thereof, and generally comprises about 40% to about 70% of acrylic acid, about 20% to about 50% of water, and about 4% to about 10%
15 of acetic acid. Further, this aqueous solution may include aldehydes such as formaldehyde, acetaldehyde, acrolein, furfural and benzaldehyde, organic acids such as propionic acid and maleic acid, and other various by-products. Removal of water from the aqueous crude acrylic acid solution can be
20 conducted in the presence of the specific substances by a conventionally known method, and for example, it can be conducted by effecting azeotropic dehydration in vacuum of about 10 kPa to about 30 kPa using an azeotropic agent such as toluene, methyl isobutyl ketone, xylene, ethylbenzene,
25 heptane and a mixture thereof. In such a dehydration method

by distillation, the concentration of water in the bottom liquid is usually 1000 ppm or less. From the top of an azeotropic dehydration column, water, acetic acid, an azeotropic agent, and components having low boiling points among by-products are usually removed by distillation. In this dehydration method by distillation, however, a part of certain components is not removed sufficiently and remains in the bottom liquid, while the components are dissolved in the water phase and are removed together with water using extraction methods.

Acrylic acid obtained by an azeotropic dehydration method, in which an aqueous crude acrylic acid solution is dehydrated by distillation to obtain a bottom liquid and then separation by distillation at lower boiling points and separation by distillation at higher boiling points are conducted, tends to have higher polymerization property as compared with that of acrylic acid obtained by an extraction method in which an aqueous crude acrylic acid solution is extracted using a mixed solvent of xylene and methyl ethyl ketone, and the like and then separation by distillation at lower boiling points and separation by distillation at higher boiling points are conducted.

However, even acrylic acid having a higher polymerization property obtained by an azeotropic dehydration method can be significantly inhibited in

polymerization, in the presence of a specific amine, particularly in the presence of a specific amine and a specific polymerization inhibitor together. The reason for this is not definite sufficiently, however, it is estimated that a trace amount of by-product(s) which can be removed in an extraction step of an extraction method remains in an azeotropic dehydration method and these remaining by-product(s) act as substance(s) promoting the polymerization, and by addition of the specific amine, these substance(s) react to become substance(s) which do not promote the polymerization. Compound(s) estimated as these substance(s) are detected by conducting an analysis of derivative(s) by 2,4-dinitrophenylhydrazine in liquid chromatography, and the remaining behavior thereof coincides with that of specific peak(s) detected together with formaldehyde, acrolein and the like in liquid chromatography. Namely, acrylic acid obtained by an extraction method does not exhibit the specific peak(s), while acrylic acid obtained by an azeotropic dehydration method exhibit the specific peak(s) and the peak(s) disappear by treatment with the amines.

Examples of the amines used in the present invention include ammonia, ammonium salts such as ammonium acetate and ammonium acrylate, aliphatic primary monoamines such as methylamine, ethylamine, propylamine, isopropylamine, n-

butylamine, sec-butylamine, tert-butylamine, n-hexylamine, cyclohexylamine, n-octylamine and 2-ethylhexylamine, aliphatic primary diamines such as ethylenediamine, trimethylenediamine, 1,4-diaminobutane and
5 hexamethylenediamine, aliphatic primary polyamines having at least one primary amine group at the end of chemical formula thereof such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 3-(methylamino)propylamine, diaminopropylamine, N-methyl-3,3'-iminobis(propylamine)
10 and pentaethylenehexamine, aromatic primary amines such as aniline, toluidine, anisidine, aminophenol and phenylenediamine, amino acids such as glycine, alanine and methionine, and alkanol amines such as monoethanolamine, diethanolamine, isopropanolamine, 3-amino-1-propanol and
15 N-(2-aminoethyl)ethanolamine. These amines may be used alone or in combination of two or more, simultaneously.

Effect of addition of amines can also be confirmed in a bottom liquid of an azeotropic dehydration column, a bottom liquid and extracted liquid of a column for separating
20 components having low boiling point, in purification process. It is estimated that the above-described substance(s) promoting polymerization of acrylic acid are already produced in an aqueous solution in the step of oxidation reaction and can not be separated sufficiently from acrylic acid by
25 distillation operation. From the stand point of reduction

of polymerization problems in whole purification process, it is desirable that the amine is added into an upper flow side, namely, into a feeding liquid or a bottom liquid of an azeotropic dehydration column, and the like.

5 The amount of amine to be added may be an amount which can treat the above-described polymerization promoting substance(s) which are estimated to exist in a trace amount, and is usually from about 0.001 to about 0.5% by weight, preferably from about 0.005 to about 0.2% by weight based on
10 acrylic acid.

 Since it is not estimated that the amine alone acts directly as a polymerization inhibitor, the amine is used together with a specific polymerization inhibitor in the present invention. As the polymerization inhibitor in the
15 present invention, a public-known inhibitor can be used which is usually used in purification of crude acrylic acid or aqueous solution thereof. Examples thereof include dibenzo-p-thiazines such as phenothiazine and methylene blue, and copper dithiocarbamates such as copper dimethyl
20 dithiocarbamate, copper diethyl dithiocarbamate, copper dipropyl dithiocarbamate and copper dibutyl dithiocarbamate. These may be used alone, or in combination of two or more, or may be used together with other polymerization inhibitors usually used for inhibiting polymerization of acrylic acid.
25 For example, it is preferred to use phenols such as phenol,

hydroquinone, p-methoxyphenol, benzoquinone, 1,2-naphthoquinone, cresol, catechol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butylphenol, 6-t-butyl-m-cresol, 2,6-di-t-butyl-p-cresol, 4-t-butylcatechol, 2,4-dimethyl-6-t-butylphenol, 2-t-butylhydroquinone and 2-t-butyl-4-methoxyphenol, together with dibenzo-p-thiazines and/or copper dithiocarbamates. Further, an oxygen-containing gas such as air may be used together. Preferably, at least one dibenzo-p-thiazine and at least one copper dithiocarbamate are used together, and more preferably, at least one other polymerization inhibitor such as phenol is also used together with dibenzo-p-thiazines and copper dithiocarbamates. The amount of such polymerization inhibitors to be used other than the amines is not particularly restricted, and is usually from about 0.0001 to about 0.5% by weight, preferably from about 0.001 to about 0.2% by weight based on acrylic acid. The addition time of these polymerization inhibitors is not particularly restricted providing that these inhibitors are contained in a crude acrylic acid or an aqueous solution thereof which is used for purification operation, and for example, they are added via reflux lines of a distillation column and the like, in which acrylic acid is present, such as a dehydration distillation column, a column for separating components having lower boiling point and a column for producing products.

As described above, according to the present invention, it is possible to effectively suppress polymerization of acrylic acid in purification by an azeotropic dehydration method by allowing the specific amine and the specific
5 polymerization inhibitor to exist even in a small amount and, therefore, the industrial utility of the present invention is extremely large.

The entire disclosure of the Japanese Patent Application No. 10-163875 filed on June 11, 1998 and the Japanese Patent
10 Application No. 10-222872 filed on August 6, 1998, both indicating specification, claims and summary, are incorporated herein by reference in their entirety.

EXAMPLE

15 The present invention is described in more detail by following Examples, which should not be construed as a limitation upon the scope of the present invention.

In the Examples, Comparative examples and Reference Example, the polymerization test was conducted as follows.

20 Polymerization test :

Five(5) g of a test sample in which concentrations of a polymerization inhibitor and amines have been adjusted to specific values was charged into a test tube equipped with a lid and having an internal volume of 20 ml. A nitrogen gas
25 containing 100 ppm oxygen was bubbled into the test sample

for 5 minutes in a nitrogen box, and the test tube was sealed and immersed in an oil bath controlled to 100°C to be heated for a specific time and, then, taken out and cooled. After this test sample was diluted with water, the produced polymer of acrylic acid in the test sample was allowed to react with a quaternary ammonium salt, and the turbidity of the sample is measured using a spectrophotometer to quantify polyacrylic acid. An increase in polyacrylic acid concentration per unit time, namely, a production rate of polyacrylic acid was calculated based on the amount of the polyacrylic acid.

Example 1

About 55% by weight of aqueous solution of acrylic acid obtained by a two-stage gas phase catalytic oxidation of propylene was dehydrated by distillation using toluene as an azeotropic agent, and then, was subjected to separation by distillation at lower boiling points and distillation at higher boiling points, to obtain acrylic acid (containing phenothiazine of 200 ppm and p-methoxyphenol of 50 ppm). Into the obtained acrylic acid, were added a 25% ammonia water and copper dibutyl dithiocarbamate to prepare a sample so that concentrations of ammonia water and copper dibutyl dithiocarbamate in the sample were 224 ppm (56 ppm in terms of ammonia) and 25 ppm, respectively. Using this sample, the polymerization test was conducted according to the above-

described method. The results are shown in Table 1.

Comparative Example 1

The same procedure of an azeotropic dehydration method as in Example 1 was conducted to obtain acrylic acid
5 (containing phenothiazine of 200 ppm and p-methoxyphenol of 50 ppm). Using the obtained acrylic acid as a sample as it was, the polymerization test was carried out. The results are shown in Table 1.

Comparative Example 2

10 The same procedure of an azeotropic dehydration method as in Example 1 was conducted to obtain acrylic acid (containing phenothiazine of 200 ppm and p-methoxyphenol of 50 ppm). Into the obtained acrylic acid, was added copper dibutyl dithiocarbamate to prepare a sample so that the
15 concentration of copper dibutyl dithiocarbamate in the sample was 25 ppm. Using this sample, the polymerization test was carried out. The results are shown in Table 1.

Reference Example

From an about 55% by weight of aqueous solution of
20 acrylic acid obtained by two-stage gas phase catalytic oxidation of propylene, was separated acrylic acid by extraction using a mixed solvent of methyl ethyl ketone and xylene to obtain an acrylic acid solution. Using this solution, separation by distillation of the extraction
25 solvents and separation by distillation at high boiling

points were conducted to obtain acrylic acid (containing phenothiazine at 200 ppm and p-methoxyphenol at 50 ppm). Using the obtained acrylic acid as a sample as it was, the polymerization test was carried out. The results are shown

5 in Table 1.

Table 1

	Sample	Polymerization inhibitor (ppm)			25% ammonia water (ppm)	Polyacrylic acid production rate (ppm/h)
		CBSC	Pz	MQ		
Example 1	Azeotropic dehydration method(*1)	25	200	50	224	272
Comparative example 1	Azeotropic dehydration method(*1)	0	200	50	0	4,436
Comparative example 2	Azeotropic dehydration method(*1)	25	200	50	0	1,493
Reference Example	Extraction method(*2)	0	200	50	0	217

(*1) Acrylic acid obtained by azeotropic dehydration method was used.

10 (*2) Acrylic acid obtained by extraction method was used.

CBSC: copper dibutyl dithiocarbamate

Pz: phenothiazine

MQ: p-methoxyphenol

15 Example 2

About 55% by weight of aqueous solution of acrylic acid obtained by two-stage gas phase catalytic oxidation of propylene was dehydrated by distillation using toluene as an

azeotropic agent to obtain a bottom liquid (containing acrylic acid of 80% by weight, toluene of 17% by weight, phenothiazine of 500 ppm, p-methoxyphenol of 150 ppm and copper dibutyl dithiocarbamate of 80 ppm). Into the obtained
 5 bottom liquid, was added 25% ammonia water to prepare a sample so that the concentration of ammonia water in the sample was 224 ppm. Using this sample, the polymerization test was conducted according to the above-described method. The results are shown in Table 2.

10 Comparative Example 3

The same procedure for an azeotropic dehydration method as in Example 2 was conducted to obtain an azeotropic dehydration bottom liquid (containing containing acrylic acid of 80% by weight, toluene of 17% by weight, phenothiazine
 15 of 500 ppm, p-methoxyphenol of 150 ppm and copper dibutyl dithiocarbamate of 80 ppm). Using the obtained bottom liquid as a sample as it was, the polymerization test was carried out. The results are shown in Table 2.

20 Table 2

	Polymerization inhibitor(ppm)			25% ammonia water (ppm)	Polyacrylic acid production rate (ppm/h)
	CBSC	Pz	MQ		
Example 2	80	500	150	224	204
Comparative Example 3	80	500	150	0	947

CBSC: copper dibutyl dithiocarbamate

Pz: phenothiazine

MQ: p-methoxyphenol

5 Examples 3 to 13

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 2 were conducted, except that aliphatic monoamines shown in Table 3 were added at the concentrations thereof shown in Table 3, respectively, instead of adding the ammonia water of Example 2. The results are shown in Table 3.

Table 3

	Aliphatic monoamine	amines concent- ration (ppm)	Polyacrylic acid production rate (ppm/h)
Example 3	Ammonium acetate	250	243
Example 4	Methylamine (40%)	250	375
Example 5	Ethylamine (70%)	210	140
Example 6	n-Propylamine	200	172
Example 7	n-Butylamine	240	152
Example 8	tert-Butylamine	240	164
Example 9	sec-Butylamine	240	147
Example 10	n-Hexylamine	330	174
Example 11	Cyclohexylamine	325	139
Example 12	n-Octylamine	420	149
Example 13	2-Ethylhexylamine	420	138

15 Examples 14 to 17

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 2 were conducted,

except that aliphatic primary diamines shown in Table 4 were added at the concentrations thereof shown in Table 4, respectively, instead of adding the ammonia water of Example 2. The results are shown in Table 4.

5

Table 4

	Aliphatic primary diamine	amines concentration (ppm)	Polyacrylic acid production rate (ppm/h)
Example 14	Ethylenediamin	200	192
Example 15	Trimethylenediamine	250	142
Example 16	1,4-Diaminobutane	290	188
Example 17	Hexamethylenediamine	380	93

Examples 18 to 24

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 2 were conducted, except that aliphatic primary polyamines shown in Table 5 were added at the concentrations thereof shown in Table 5, respectively, instead of adding the ammonia water of Example 2. The results are shown in Table 5.

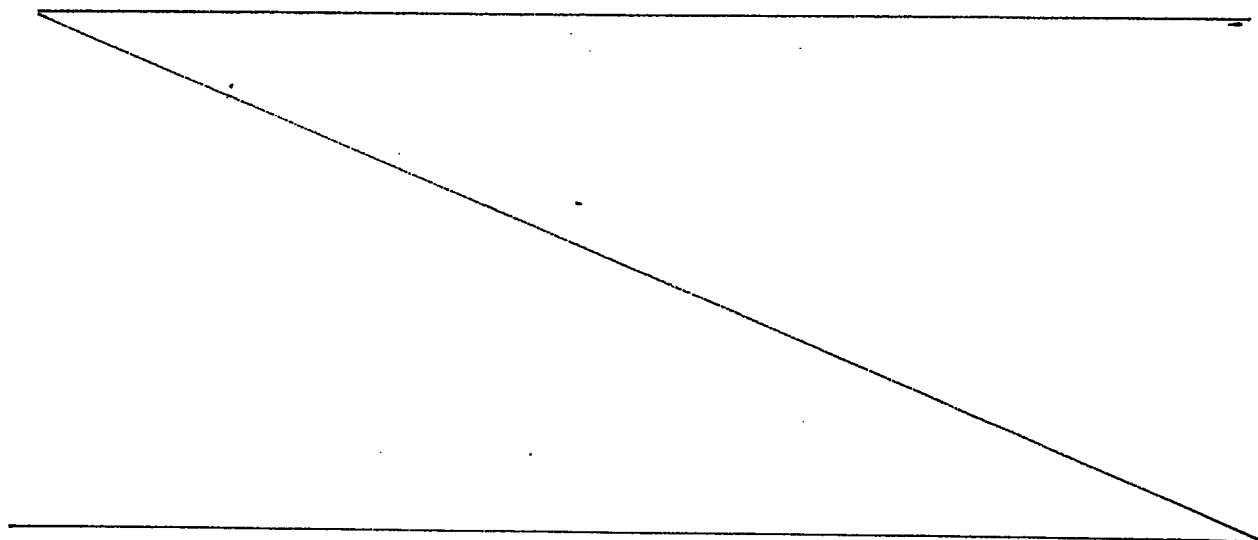


Table 5

	Aliphatic primary polyamine	amines concentration (ppm)	Polyacrylic acid production rate (ppm/h)
Example 18	Diethylenetriamine	340	161
Example 19	Triethylenetetramine	480	78
Example 20	Tetraethylenepentamine	620	82
Example 21	3-Methylaminopropylamine	290	122
Example 22	3,3'-Diaminodipropylamine	430	171
Example 23	N-methyl-3,3'-iminobis(propylamine)	480	71
Example 24	Pentaethylenehexamine	760	44

Examples 25 to 29

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 2 were conducted, except that aromatic primary amines shown in Table 6 were added at the concentrations thereof shown in Table 6, respectively, instead of adding the ammonia water of Example 2. The results are shown in Table 6.

10

Table 6

	Aromatic primary amine	amines concentration (ppm)	Polyacrylic acid production rate (ppm/h)
Example 25	Aniline	300	404
Example 26	Toluidine	350	326
Example 27	Anisidine	430	384
Example 28	Aminophenol	360	291
Example 29	Phenylenediamine	350	107

Examples 30 to 32

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 2 were conducted, except that amino acids shown in Table 7 were added at the concentrations thereof shown in Table 7, respectively,
 5 instead of adding the ammonia water of Example 2. The results are shown in Table 7.

Table 7

	Amino acid	amines concent- ration (ppm)	Polyacrylic acid production rate (ppm/h)
Example 30	Glycine	250	275
Example 31	Alanine	290	241
Example 32	Methionine	490	282

10 Example 33

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 1 were conducted, except that monoethanolamine was added so that the concentration thereof was 200 ppm, instead of adding ammonia
 15 water. Polyacrylic acid production rate was 163 ppm/h.

Example 34

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 2 were conducted, except that monoethanolamine was added so that the
 20 concentration thereof was 200 ppm, instead of adding ammonia water. Polyacrylic acid production rate was 73 ppm/h.

Examples 35 to 38

The same procedures for an azeotropic dehydration method and a polymerization test as in Example 2 were conducted, except that alkanolamines shown in Table 8 were added at the concentrations thereof shown in Table 8, respectively, instead of adding the ammonia water of Example 2. The results are shown in Table 8.

Table 8

	Alkanolamine	amines concent- ration (ppm)	Polyacrylic acid production rate (ppm/h)
Example 35	Diethanolamine	345	59
Example 36	Isopropanolamine	437	78
Example 37	3-Amino-1-propanol	246	108
Example 38	N-(2-aminoethyl)ethanolamine	342	111

What is claimed is:

1. A method for producing acrylic acid comprising a step of catalytically oxidizing propylene and/or acrolein in gas phase by using a molecular oxygen-containing gas to obtain
5 an aqueous crude acrylic acid solution, and a step of dehydrating the solution by distillation in the presence of (i) at least one moiety selected from ammonia, ammonium salts, aliphatic primary monoamines, aliphatic primary diamines, aliphatic primary polyamines, aromatic primary amines, amino
10 acids and alkanolamines, and (ii) at least one moiety selected from dibenzo-p-thiazines and copper dithiocarbamates.

2. A method according to Claim 1, wherein said step of dehydrating said aqueous crude acrylic acid solution by distillation is conducted in the presence of at least one
15 moiety selected from phenol, hydroquinone, p-methoxyphenol, benzoquinone, 1,2-naphthoquinone, cresol, catechol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butylphenol, 6-t-butyl-m-cresol, 2,6-di-t-butyl-p-cresol, 4-t-butylcatechol, 2,4-dimethyl-6-t-butylphenol, 2-t-butylhydroquinone and
20 2-t-butyl-4-methoxyphenol.

3. A method according to Claim 1 or 2, wherein said step of dehydrating said aqueous crude acrylic acid solution by distillation is conducted in the presence of both of at least one dibenzo-p-thiazine and at least one copper
25 dithiocarbamate.



4. A method according to any one of Claims 1 to 3,
wherein in said step of dehydrating said aqueous crude acrylic
acid solution by distillation, the amount of ammonia,
ammonium salt, aliphatic primary monoamines, aliphatic
5 primary diamines, aliphatic primary polyamines, aromatic
primary amines, amino acids and alkanolamines is about 0.001
by weight to about 0.5% by weight based on acrylic acid.

5. A method according to any one of Claims 1 to 4,
wherein in said step of dehydrating said aqueous crude acrylic
10 acid solution by distillation, at least one moiety selected
from ammonia, ammonium salt, aliphatic primary monoamines,
aliphatic primary diamines, aliphatic primary polyamines,
aromatic primary amines, amino acids and alkanolamines is
added to a feeding liquid or a bottom liquid of an azeotropic
15 dehydration column.

6. A method for inhibiting the polymerization of
acrylic acid which comprises providing a mixture or solution
of acrylic acid that additionally contains (i) at least one
moiety selected from ammonia, ammonium salts, aliphatic
20 primary monoamines, aliphatic primary diamines, aliphatic
primary polyamines, aromatic primary amines, amino acids and
alkanolamines, and (ii) at least one moiety selected from
dibenzo-p-thiazines and copper dithiocarbamates.

7. A method for purifying acrylic acid in which
25 distillation of acrylic acid is conducted in the presence of



(i) at least one moiety selected from ammonia, ammonium salts, aliphatic primary monoamines, aliphatic primary diamines, aliphatic primary polyamines, aromatic primary amines, amino acids and alkanolamines, and (ii) at least one moiety selected
5 from dibenzo-p-thiazines and copper dithiocarbamates.

