SPECIFICATION

PROCESS FOR PRODUCING QUATERNARY SALT OF DIALKYLAMINOALKYL (METH)ACRYLATE

[TECHNICAL FIELD]

[0001]

The present invention relates to a continuous production process for a quaternary salt of a dialkylaminoalkyl (meth)acrylate excellent in productivity.

[BACKGROUND ART]

[0002]

A quaternary salt of a dialkylaminoalkyl (meth)acrylate is produced by reacting a dialkylaminoalkyl (meth)acrylate with a quaternizing agent such as methyl chloride. As the production process, processes disclosed in the following Patent Documents 1-5 are known.

[0003]

In the conventional production processes, a method of using starting materials including a method of supplying the starting materials is devised. For example, in the method disclosed in Patent Document 1, an alkyl halide is directly introduced through an introduction tube made of glass having an inner diameter of 6 mm into a solution of only a dialkylaminoalkyl (meth)acrylate or a mixed solution containing a dialkylaminoalkyl (meth)acrylate, and water is introduced through an introduction tube with progress of the reaction. According to this method, bubbles of the introduced alkyl halide are large and might be emitted into a gas phase without being reacted.

[0004]

Patent Document 2 discloses a method for the production of a quaternary salt of a dimethylaminoalkyl (meth) acrylate, which is characterized in that a dimethylaminoalkyl (meth)acrylate, a quaternizing agent and water are continuously supplied to a reactor containing an aqueous solution of a quaternary salt of a dimethylaminoalkyl (meth)acrylate and that the reaction solution in the reactor is continuously discharged.

Patent Document 3 discloses a production method, which is characterized in that a dialkylaminoalkyl (meth)acrylate is

supplied to a reactor at a rate from 0.06% to 1.1% by weight based on a weight of the reaction solution in the reactor when a quaternary salt of a dialkylaminoalkyl (meth)acrylate is produced by supplying a dialkylaminoalkyl (meth)acrylate, a quaternizing agent having a boiling point of 25°C or lower, and water into a reactor containing an aqueous solution of a quaternary salt of dialkylaminoalkyl (meth)acrylate, and a reaction is initiated under a condition that a mass transfer capacity coefficient measured using water is 10 (1/h) or more.

In these processes, the inside of the reactor is pressurized so that a retained amount of the quaternizing agent is not lowered, but in order to prevent emission of an unreacted quaternizing agent from the aqueous solution, a finishing tank is disposed after a reaction tank, by which reaction of the unreacted quaternizing agent is promoted and loss of the quaternizing agent is reduced.

[0005]

Patent Document 4 discloses a technique of the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate under a specific condition with an amount and a rate of the quaternizing agent to be supplied, and recovery and removal of an unreacted quaternizing agent.

In addition, Patent Document 5 discloses a method in which adding condition of water is limited when a quaternary salt of a dialkylaminoalkyl (meth)acrylate is produced by adding a vinyl monomer such as a dialkylaminoalkyl (meth)acrylate and water separately to a quaternizing agent.

[0006]

[Patent Document 1] JP-A 2005-220111

[Patent Document 2] JP-A 2003-342244

[Patent Document 3] JP-A 2004-10508

[Patent Document 4] JP-A S63-5064

[Patent Document 5] JP-A H3-135945

[DISCLOSURE OF THE INVENTION]

[PROBLEMS THAT THE INVENTION IS TO SOLVE]

[0007]

When a quaternary salt of a dialkylaminoalkyl (meth)acrylate is produced, a quaternizing agent is excessively used to a dialkylaminoalkyl (meth)acrylate in usual in order to prevent decreasing yield. However, methyl chloride generally used as a

quaternizing agent is a substance subjected to PRTR Law (Law for Pollutant Release and Transfer Register), and its emission in a large quantity to a gas phase is not desirable from the viewpoints of environmental contamination, safety in work and the like. In addition, when the production method has a process for recovering the quaternizing agent in order to reuse, there may be a problem that extra operations such as concentration control thereof is needed. Moreover, in the case where the production in an aqueous solution of a quaternary salt of a dialkylaminoalkyl (meth)acrylate is performed as in Patent Documents 2 and 3, while the quaternizing agent is moved to a gas phase, a dialkylaminoalkyl (meth)acrylate is hydrolyzed in the aqueous solution, and there is a problem that acrylic acid is generated in a large quantity.

[0008]

The present invention has an object to provide a continuous production process for a quaternary salt of a dialkylaminoalkyl (meth)acrylate excellent in productivity while reaction efficiency of a quaternizing agent is improved and generation of acrylic acid as a by-product is inhibited when the quaternary salt of a dialkylaminoalkyl (meth)acrylate by reacting a dialkylaminoalkyl (meth)acrylate with a gaseous quaternizing agent such as methyl chloride, which is a chemical substance subjected to the PRTR Law in an aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate.

[MEANS FOR SOLVING THE PROBLEMS]

[0009]

The present invention is as follows.

1. A process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate in which a dialkylaminoalkyl (meth)acrylate, a gaseous quaternizing agent and water are fed to an aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate in a reactor to react the dialkylaminoalkyl (meth)acrylate and the quaternizing agent, characterized in that the quaternizing agent is continuously fed in the form of a bubble having an average diameter of 100 μm or smaller, and that a molar ratio of the quaternizing agent to be used is in the range from 1 to 1.2 based on the dialkylaminoalkyl (meth)acrylate to be used.

2. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to 1 above, wherein a

concentration of the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate in the reactor is in the range from 30% to 90% by weight.

3. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to 1 or 2 above, wherein a pressure in the reactor is in the range from an atmospheric pressure to 1 MPaG.

4. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to any one of 1 to 3 above, wherein a content of an acrylic acid generated as a by-product is less than 1,000 ppm by weight.

5. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to 1 above, wherein the quaternizing agent is methyl chloride, wherein the dimethylaminoethyl (meth)acrylate is a dialkylaminoalkyl (meth)acrylate, wherein the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the reactor is a chloride, wherein a concentration of the chloride is in the range from 60% to 85% by weight, and wherein a molar ratio of the quaternizing agent to be used is in the range from 1 to 1.1 based on the dialkylaminoalkyl (meth)acrylate to be used.

6. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to 1 above, wherein the quaternizing agent is methyl chloride, wherein the dimethylaminoethyl (meth)acrylate is a dialkylaminoalkyl (meth)acrylate, wherein the average diameter of the bubble is 80 μm or smaller, wherein the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the reactor is a chloride, wherein a concentration of the chloride is in the range from 70% to 85% by weight, wherein a molar ratio of the quaternizing agent to be used is in the range from 1 to 1.05 based on the dialkylaminoalkyl (meth)acrylate to be used, and wherein a concentration of the quaternary salt of a dialkylaminoalkyl (meth)acrylate to be produced is lower than a concentration of the quaternary salt of the dialkylaminoalkyl (meth)acrylate in the reactor, and is in the range from 50% to 82% by weight.

[EFFECT OF THE INVENTION]

[0010]

According to the present invention, a quaternary salt of a dialkylaminoalkyl (meth)acrylate can be continuously produced while generation of acrylic acid as a by-product is inhibited. Since a content of acrylic acid generated as a by-product can be kept to less than 1,000 ppm by weight and reaction efficiency of the gaseous quaternizing agent can be improved in particular, the production process is excellent in productivity of the quaternary salt of the dialkylaminoalkyl (meth)acrylate. The gaseous quaternizing agent such as methyl chloride generally used is a substance subjected to the PRTR Law, however, an emission to the gas phase can be drastically reduced and moreover inhibited by the production process according to the present invention, which is advantageous from the viewpoints of environmental contamination, safety in work and the like.

In the case where the concentration of the quaternary salt of the dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate in the reactor is in the range from 30% to 90% by weight, the reaction efficiency of the gaseous quaternizing agent can be improved, which is suitable for continuous production of the quaternary salt of the dialkylaminoalkyl (meth)acrylate.

In the case where the pressure in the reactor is in the range from an atmospheric pressure to 1 MPaG (atmospheric pressure or more and 1 MPaG or less), a dissolved amount of the quaternizing agent in the aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate is increased and its retention in the solution can be further extended, by which emission to the gas phase can be inhibited, reaction with the quaternary salt of the dialkylaminoalkyl (meth)acrylate is promoted, and almost all the quaternizing agent supplied to the aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate can be used for the reaction with the dialkylaminoalkyl (meth)acrylate.

In the case where the quaternizing agent is methyl chloride, the dialkylaminoalkyl (meth)acrylate is dimethylaminoethyl (meth)acrylate, the quaternary salt of the dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate contained in the reactor is a chloride, the concentration of the chloride is in the range from

60% to 85% by weight, and the amount of the quaternizing agent to be used is 1 to 1.1 times (molar ratio) to the amount of the dialkylaminoalkyl (meth)acrylate to be used, the reaction efficiency of the quaternizing agent can be improved, generation of acrylic acid as a by-product is inhibited, and the quaternary salt of the dialkylaminoalkyl (meth)acrylate can be continuously produced, being excellent productivity.

In the case where the quaternizing agent is methyl chloride, the dimethylaminoethyl (meth)acrylate is a dialkylaminoalkyl (meth)acrylate, the average diameter of the bubble is 80 μm or smaller, the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the reactor is a chloride, the concentration of the chloride is in the range from 70% to 85% by weight, the amount of the quaternizing agent to be used is 1 to 1.05 times (molar ratio) to the amount of the dialkylaminoalkyl (meth)acrylate to be used, and the concentration of the quaternary salt of a dialkylaminoalkyl (meth)acrylate to be produced is lower than a concentration of the quaternary salt of the dialkylaminoalkyl (meth)acrylate in the reactor, and is in the range from 50% to 82% by weight, the reaction efficiency of the quaternizing agent can be improved, generation of acrylic acid as a by-product is inhibited, and the quaternary salt of the dialkylaminoalkyl (meth)acrylate can be continuously produced, being excellent productivity.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0011]

Fig. 1 is a schematic diagram illustrating an example of a production apparatus according to the process of the present invention.

[EXPLANATION OF THE REFERENCE NUMBERS]

[0012]

1: production apparatus, 11: reactor, 12: micro bubble generator, 13: quaternizing agent storage part, 15: dialkylaminoalkyl (meth)acrylate supplying pipe, 16: water supplying pipe, 17: agitator, 19: DAM aqueous solution transfering pipe, 2: bubble (quaternizing agent)

[BEST MODE FOR CARRYING OUT THE INVENTION]

[0013]

The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate (hereinafter, also referred to as "DAM") of the present invention (hereinafter, referred to as "production process of the present invention") is characterized in that the quaternizing agent is continuously fed in the form of a bubble having an average diameter of 100 μm or smaller, and that a molar ratio of the quaternizing agent to be used is in the range from 1 to 1.2 based on the dialkylaminoalkyl (meth)acrylate to be used in a dialkylaminoalkyl (meth)acrylate, a gaseous quaternizing agent and water are fed to an aqueous solution of the quaternary salt of the dialkylaminoalkyl (meth)acrylate (hereinafter, also referred to as "DAM aqueous solution") in a reactor to react the dialkylaminoalkyl (meth)acrylate and the quaternizing agent.

It is noted that "(meth)acrylate" means acrylate and methacrylate in the specification.

[0014]

In the preferable production process of the present invention, a gaseous quaternizing agent is continuously supplied to a DAM aqueous solution in a reactor and a dialkylaminoalkyl (meth)acrylate and water are supplied continuously or dividedly.

Examples of the dialkylaminoalkyl (meth)acrylate include dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, di-n-propylaminoethyl (meth)acrylate, di-isopropylaminoethyl (meth)acrylate and the like. These compounds may used singly or in combination of two or more types thereof. In the present invention, dimethylaminoethyl (meth)acrylate is preferable.

The quaternizing agent is preferably a compound having a boiling point at 1 atmospheric pressure of 50°C or lower, and the more preferable is a compound of -30°C to 30°C. Examples of the compound having a boiling point of 50°C or lower include methyl chloride (b.p. -24.2°C), ethyl chloride (b.p. 12.3°C), n-propyl chloride (b.p. 46.6°C), isopropyl chloride (b.p. 38.8°C) and the like. These compounds may be used singly or in combination of two or more types thereof. In the present invention, methyl chloride, which is gas at a normal temperature, is preferable.

In addition, water is preferably used in which the metal components are rarely contained, and distilled water or ion-exchanged water is usually used.

[0015]

Type of the DAM contained in the DAM aqueous solution is not particularly limited, and the same DAM as the DAM to be produced is used in usual. That is, when the DAM to be produced is methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate, the DAM contained in the DAM aqueous solution is the same compound (methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate). As a starting material in this case, dimethylaminoethyl (meth)acrylate is used as the dialkylaminoalkyl (meth)acrylate, and methyl chloride is used as the quaternizing agent.

Additionally, the concentration of the DAM in the DAM aqueous solution is not particularly limited, and is preferably in the range from 30% to 90% by weight, more preferably from 60% to 85% by weight, and further preferably from 70% to 85% by weight. When the DAM concentration is within this range, the DAM can be produced with high reaction efficiency.

[0016]

In the production process of the present invention, the DAM aqueous solution is contained in a reactor in advance. It may be so configured that when a reaction starts, that is, when the dialkylaminoalkyl (meth)acrylate, gaseous quaternizing agent and water are started to be supplied, an additional DAM aqueous solution may be supplied continuously or dividedly while the DAM concentration in the reactor is maintained in the preferable range. The DAM aqueous solution used at this time is preferably the same aqueous solution (aqueous solution containing the same type of DAM) as the contained DAM aqueous solution in advance or an aqueous solution with a higher concentration (aqueous solution containing the same type of DAM).

In the case of supplying the dialkylaminoalkyl (meth)acrylate, gaseous quaternizing agent and water to the reactor in a state where the DAM aqueous solution is not contained in advance for reaction, the dimethylaminoacryl (meth)acrylate may be hydrolyzed to generate (meth)acrylic acid, and the purity of the DAM in the obtained reaction solution may be lowered.

[0017]

The reactor is arbitrarily selected so long as it has heat resistance and corrosion resistance. Additionally its material, structure or size is not particularly limited. The preferable reactor is one in which an inner surface thereof is subjected to

coating and/or lining with glass or the like. Moreover, since the gaseous quaternizing agent is used, a reactor having a structure with excellent air-tightness is preferable, and one having a structure capable of pressurization is more preferably. Example thereof includes an autoclave and the like.

The reactor may be provided with, as will be described later, an agitator for agitating starting material and the like, a micro bubble generator for supplying the gaseous quaternizing agent, and the like.

[0018]

In the production process of the present invention, the quaternizing agent is continuously supplied in the form of a bubble having an average diameter of 100 μm or smaller, preferably 95 μm or smaller, and further preferably 80 μm or smaller into the DAM aqueous solution. A lower limit of the average diameter of bubbles is usually 1 μm. When the quaternizing agent having the above average diameter is used, a rising speed of the bubbles is delayed in the DAM aqueous solution, and the quaternizing agent becomes difficult to be emitted to the gas phase. As a result, the retention time of the quaternizing agent in the DAM aqueous solution can be extended, and the DAM can be produced with high reaction efficiency. The average diameter can be measured by visual check, a light scattering method using laser or the like, and the like.

[0019]

The method for the formation of bubbles using the quaternizing agent is not particularly limited. Only the quaternizing agent may be used for that or this quaternizing agent and water may be used in combination to form bubbles. Examples of generating means of bubbles by the micro bubble generator include a gas-liquid two-phase swirl method, an ejector method and the like.

The bubbles may be supplied from any direction. That is, the bubbles may be supplied from any of above, side and below the DAM aqueous solution contained in the reactor. Therefore, the micro bubble generator may be disposed at any position of the reactor.

[0020]

The supplying rate of the quaternizing agent is appropriately selected depending on to the concentration and amount of the DAM aqueous solution contained in the reactor, a capacity of the reactor and the like. It is usually in the range from 25 to

400 grams per hour, and preferably from 100 to 200 grams per hour based on 1 liter of the DAM aqueous solution or a reaction solution to be produced. Within this range, the quaternizing agent is difficult to be emitted to the gas phase, and the DAM can be produced with high reaction efficiency.

[0021]

The dialkylaminoalkyl (meth)acrylate and water is preferably supplied continuously or dividedly rather than wholly in order to prevent a composition of the reaction system from being unstable over time.

The supplying rates of the dialkylaminoalkyl (meth)acrylate and water are not particularly limited. The supplying rate of the dialkylaminoalkyl (meth)acrylate is usually in the range from 50 to 1,200 grams per hour, and preferably from 200 to 600 grams per hour based on 1 liter of the DAM aqueous solution or a reaction solution to be produced. It is noted that the reaction of the dialkylaminoalkyl (meth)acrylate and quaternizing agent used for producing the DAM is an equimolar reaction. However, in order that the reactions are further promoted with higher reaction efficiency and that the quaternizing agent should be present at high concentration in the reaction solution even if a part of the quaternizing agent is emitted from the reaction solution to the gas phase, an amount (cumulative supply amount) of the quaternizing agent to be used should be equal to or larger than the amount (cumulative supply amount) of the dialkylaminoalkyl (meth)acrylate to be used in terms of molar ratio, and the molar ratio is set to the range from 1 to 1.2, preferably 1 to 1.1, and more preferably 1 to 1.05. Within this range, productivity, quality and safety are excellent.

Additionally, the supplying rate of water is usually in the range from 25 to 400 grams per hour, and preferably from 100 to 200 grams per hour based on 1 liter of the DAM aqueous solution or a reaction solution to be produced. When the reaction progresses to produce the DAM, the DAM concentration in the reaction solution is changed. When the water is supplied according to a purpose, an application and the like at this time, the DAM concentration can be adjusted.

In the preferable production process of the present invention, the dialkylaminoalkyl (meth)acrylate, the quaternizing agent and water are supplied so that the DAM concentration in the

reaction solution to be obtained is equal to or lower than the DAM concentration in the DAM aqueous solution contained in advance before the reaction by preferably 1% to 5% by weight, and more preferably 2% to 4% by weight. As a result, the DAM aqueous solution can be produced in which content of acrylic acid produced as a by-product is inhibited.

[0022]

In the production process of the present invention, a reaction temperature is appropriately selected depending on the type of the dialkylaminoalkyl (meth)acrylate, the type of the quaternizing agent used for production of the DAM, and the like. It is usually in the range from 30°C to 60°C, and preferably from 40°C to 60°C. The DAM aqueous solution contained in the reactor in advance, and the dialkylaminoalkyl (meth)acrylate and water as the starting material may be heated to the above temperature for use.

The pressure in the reactor is preferably in the range from the atmospheric pressure to 1 MPaG. As a result, the quaternizing agent can be retained in the DAM aqueous solution for longer time, and emission thereof to the gas phase can be inhibited. The pressure is more preferably in the range from 0.05 to 0.7 MPaG, and further preferably from 0.1 to 0.5 MPaG.

[0023]

According to the production process of the present invention, generation of acrylic acid as a by-product is inhibited and the content of the acrylic acid in the obtained DAM aqueous solution is usually less than 1,000 ppm by weight, preferably less than 900 ppm by weight, and more preferably less than 700 ppm by weight. Since the quaternizing agent as a starting material scarcely remains, the DAM aqueous solution with high purity at less content of components other than the DAM can be obtained by the production process of the present invention. The DAM concentration in the obtained DAM aqueous solution is usually in the range from 50% to 85% by weight, and preferably from 50% to 82% by weight.

[0024]

In the production process of the present invention, the DAM aqueous solution (reaction solution) in the reactor is preferably discharged with production of the DAM. This discharge of the DAM aqueous solution may be started at the same time as the start of supply of the starting material or may be started after a predetermined time has elapsed since the starting material was

supplied. In these cases, the method and condition for discharging are not particularly limited. The discharge may be performed continuously or intermittently. When the discharge amount of the DAM aqueous solution is adjusted according to the supply amount of the starting material, production of the DAM and discharge of the aqueous solution can be performed at a constant rate. In this case, the DAM aqueous solution having a stable DAM concentration during production and a reduced content of the by-product can be produced continuously in the reactor.

[0025]

The discharged DAM aqueous solution is contained in a storage tank or the like, and oxygen dissolution processing is performed using an oxygen-containing gas as necessary. By means of this processing, polymerization of the DAM can be prevented. In the case of remaining an unreacted quaternizing agent in the DAM aqueous solution, the quaternizing agent can be removed. This oxygen-containing gas may be introduced into a gas-phase portion in the storage tank or bubbled in the DAM aqueous solution. Both works may be performed simultaneously or alternately. In order to efficiently remove the quaternizing agent remaining in the DAM aqueous solution, the oxygen-containing gas is preferably bubbled into the DAM aqueous solution.

As the oxygen-containing gas, oxygen gas or a mixed gas of air and inert gas such as nitrogen gas and argon gas is usually used. Introduction conditions of the oxygen-containing gas such as introducing amount, introducing time, temperature of the DAM aqueous solution, and the like) are not particularly limited.

The inner pressure of the storage tank or the like is preferably in the range from the atmospheric pressure to 0.7 MPaG (atmospheric pressure or more and 0.7 MPaG or less). Within the range, polymerization of the DAM can be prevented.

[0026]

The preferable producing method in the present invention is one having following conditions in which the quaternizing agent is methyl chloride; the dimethylaminoethyl (meth)acrylate is a dialkylaminoalkyl (meth)acrylate; the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the reactor is a chloride; the concentration of the chloride is in the range from 60% to 85% by weight; and the molar ratio of the

quaternizing agent to be used is in the range from 1 to 1.1 based on the dialkylaminoalkyl (meth)acrylate to be used. According to this method, the reaction efficiency can be improved without supplying the quaternizing agent (methyl chloride) more than necessary. Additionally, the DAM aqueous solution having a content of acrylic acid less than 1,000 ppm by weight can be produced continuously and stably. In the case where the DAM aqueous solution (reaction solution) in the reactor is discharged, the above effects can be further improved. Therefore, this production process inhibits emission of the quaternizing agent such as methyl chloride to the gas phase and has excellent safety, quality and productivity.

[0027]

Further, the preferable producing method in the present invention is one having following conditions in which the quaternizing agent is methyl chloride; the dimethylaminoethyl (meth)acrylate is a dialkylaminoalkyl (meth)acrylate; the average diameter of the bubble is 80 μm or smaller; the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the aqueous solution of the quaternary salt of a dialkylaminoalkyl (meth)acrylate in the reactor is a chloride; the concentration of the chloride is in the range from 70% to 85% by weight; the molar ratio of the quaternizing agent to be used is in the range from 1 to 1.05 based on the dialkylaminoalkyl (meth)acrylate to be used; the concentration of the quaternary salt of a dialkylaminoalkyl (meth)acrylate to be produced is lower than the concentration of the quaternary salt of the dialkylaminoalkyl (meth)acrylate in the reactor, and is in the range from 50% to 82% by weight. According to this method, the reaction efficiency can be improved without supplying the quaternizing agent (methyl chloride) more than necessary. Additionally, the DAM aqueous solution having a content of acrylic acid less than 1,000 ppm by weight can be produced continuously and stably. In the case where the DAM aqueous solution (reaction solution) in the reactor is discharged, the above effects can be further improved. Therefore, this production process inhibits emission of the quaternizing agent such as methyl chloride to the gas phase and has excellent safety, quality and productivity.

[0028]

An example of a production apparatus used in the production process of the present invention is shown in Fig.1. The production apparatus 1 shown in Fig.1 is provided with a reactor 11, a micro bubble generator 12 disposed in the vicinity of an inner-part bottom face of the reactor 11, a dialkylaminoalkyl (meth)acrylate supplying pipe 15, a water supplying pipe 16, and an agitator 17. Moreover, a quaternizing agent storage part 13 for supplying a quaternizing agent to the micro bubble generator 12, a DAM aqueous solution transfering pipe 19 for discharging the DAM aqueous solution obtained by the reaction and the like can be provided.

[Example]

[0029]

Hereinafter, the present invention is concretely explained with reference to Examples. The present invention is in no way limited by these Examples.

[0030]

Example 1

A reactor in use is a vertical autoclave provided with a micro bubble generator for generating methyl chloride gas in a micronized bubble state from the bottom side to a direction of a liquid level in the reactor, an agitator, a thermometer, a pressure meter, and a jacket for temperature control.

First, 517 grams of an aqueous solution of methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate having a concentration of 82% by weight was charged into the autoclave and was heated in a sealed state of the autoclave.

After that, methyl chloride gas, dimethylaminoethyl acrylate and water were supplied to the aqueous solution at rates of 72.8 grams per hour, 206.2 grams per hour and 69.8 grams per hour, respectively while holding the aqueous solution at a temperature of 50°C, agitating, and confirming that the pressure in the autoclave was kept at the atmospheric pressure. At the same time, the aqueous solution in the autoclave was discharged at a rate of 348.8 grams per hour and was transferred to a storage tank. The aqueous solution containing the methyl chloride gas in bubble state was sampled, and an average diameter of the bubble was measured by a laser nano particle diameter distribution measuring device and was 39 μm. It was confirmed that the methyl chloride gas was rarely emitted to the gas phase in the course of the reaction.

Six hours after the starting of the supplying of the components, each cumulative supply amount of methyl chloride gas, dimethylaminoethyl acrylate and water were measured to be 437 grams (8.66 mol), 1,237 grams (8.64 mol) and 419 grams, respectively. (A molar ratio of methyl chloride to dimethylaminoethyl acrylate was 1.002.)

Six hours after the starting of the supplying of the components, the aqueous solution in the autoclave was analyzed. The concentration of the methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate was 80.1% by weight. The concentration of acrylic acid generated as a by-product was 676 ppm by weight.

[0031]

Example 2

The methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate was produced in six hours similarly to Example 1 except that the pressure in the autoclave was kept at 0.5 MPaG. The concentration of the product was 80.4% by weight, and the concentration of acrylic acid generated as a by-product was 426 ppm by weight.

[0032]

Example 3

The methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate was produced in six hours similarly to Example 1 except that the average diameter of the bubble in the reaction solution of methyl chloride gas was 90 μm. The concentration of the product was 80.2% by weight, and the concentration of acrylic acid generated as a by-product was 933 ppm by weight.

[0033]

Comparative Example 1

Using the same production apparatus as that in Example 1, 517 grams of an aqueous solution of methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate having a concentration of 82% by weight was charged into the autoclave and was heated in a sealed state of the autoclave.

After that, methyl chloride gas having average diameter of the bubble of 39 μm, dimethylaminoethyl acrylate and water were supplied to the aqueous solution at rates of 43.3 grams per hour, 128.4 grams per hour and 40.3 grams per hour, respectively while

holding the aqueous solution at a temperature of 50°C, agitating, and confirming that the pressure in the autoclave was kept at the atmospheric pressure. At the same time, the aqueous solution in the autoclave was discharged at a rate of 212.0 grams per hour and was transferred to a storage tank. It was confirmed that the methyl chloride gas was rarely emitted to the gas phase in the course of the reaction.

Six hours after the starting of the supplying of the components, each cumulative supply amount of methyl chloride gas, dimethylaminoethyl acrylate and water were measured to be 260 grams (5.15 mol), 770.2 grams (5.38 mol) and 241.7 grams, respectively. (A molar ratio of methyl chloride to dimethylaminoethyl acrylate was 0.957.)

Six hours after the starting of the supplying of the components, the aqueous solution in the autoclave was analyzed. The concentration of the methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate was 81.0% by weight. The concentration of acrylic acid generated as a by-product was 4,489 ppm by weight.

[0034]

Comparative Example 2

Using the same production apparatus as that in Example 1, 517 grams of an aqueous solution of methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate having a concentration of 82% by weight was charged into the autoclave and was heated in a sealed state of the autoclave.

After that, methyl chloride gas having average diameter of the bubble of 39 μm, dimethylaminoethyl acrylate and water were supplied to the aqueous solution at rates of 80 grams per hour, 128.4 grams per hour and 43.4 grams per hour, respectively while holding the aqueous solution at a temperature of 50°C, agitating, and confirming that the pressure in the autoclave was kept at 0.5 MPaG. At the same time, the aqueous solution in the autoclave was discharged at a rate of 251.8 grams per hour and was transferred to a storage tank. It was confirmed that the methyl chloride gas was emitted to the gas phase in the course of the reaction.

Six hours after the starting of the supplying of the components, each cumulative supply amount of methyl chloride gas, dimethylaminoethyl acrylate and water were measured to be 480 grams (9.51 mol), 770.2 grams (5.38 mol) and 260.5 grams, respectively.

(A molar ratio of methyl chloride to dimethylaminoethyl acrylate was 1.768.)

Six hours after the starting of the supplying of the components, the aqueous solution in the autoclave was analyzed. The concentration of the methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate was 79.8% by weight. The concentration of acrylic acid generated as a by-product was 430 ppm by weight.

[0035]

Comparative Example 3

517 grams of an aqueous solution of methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate having a concentration of 82% by weight was charged into the autoclave provided with a gas supplying apparatus for supplying methyl chloride gas from a nozzle having an inner diameter of approximately 2 mm, an agitator, a thermometer, a pressure meter and a jacket for temperature control, and was heated in a sealed state of the autoclave.

After that, methyl chloride gas, dimethylaminoethyl acrylate and water were supplied to the aqueous solution at rates of 80 grams per hour, 206.2 grams per hour and 69.7 grams per hour, respectively while holding the aqueous solution at a temperature of 50°C, agitating, and confirming that the pressure in the autoclave was kept at 0.5 MPaG. At the same time, the aqueous solution in the autoclave was discharged at a rate of 355.9 grams per hour and was transferred to a storage tank. The diameter of the supplied methyl chloride gas from the nozzle was visually observed and it was found to be approximately 1 mm. It was confirmed that the methyl chloride gas was emitted to the gas phase in the course of the reaction.

Six hours after the starting of the supplying of the components, each cumulative supply amount of methyl chloride gas, dimethylaminoethyl acrylate and water were measured to be 480 grams (9.51 mol), 1,237 grams (8.64 mol) and 418.3 grams, respectively. (A molar ratio of methyl chloride to dimethylaminoethyl acrylate was 1.101.)

Six hours after the starting of the supplying of the components, the aqueous solution in the autoclave was analyzed. The concentration of the methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate was 80.1% by weight. The

concentration of acrylic acid generated as a by-product was 2,205 ppm by weight.

[0036]

Comparative Example 4

Using the same production apparatus as that in Example 1, 614.2 grams (4.29 mol) of dimethylaminoethyl acrylate was charged into the autoclave and was heated to a temperature of 50°C in a sealed state of the autoclave.

After that, the liquid was held at a temperature of 50°C and agitated, and internal pressure of the sealed autoclave was pressurized to 0.5 MPaG.

Methyl chloride was continuously supplied at a rate of 1.32 grams per minute for 3 hours and at an amount consumed by reaction while keeping the pressure in the autoclave at 0.5 MPaG.

Thirty minutes after the starting of the supplying of methyl chloride, supplying of water was started at the rate of 1.38 grams per minute continuously over 2.5 hours.

Three hours after the starting of the supplying of methyl chloride, the methyl chloride in the autoclave was discharged through an outlet. Cumulative supply amount of the methyl chloride so far was 238.3 grams (4.72 mol).

Subsequently, air was blown into the autoclave for 3 hours, and excessive methyl chloride dissolved in the reaction solution was removed so as to obtain an aqueous solution of the methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate. In this aqueous solution, the concentration of the methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate was 79.9% by weight, and the concentration of acrylic acid generated as a by-product was 3,104 ppm by weight.

[INDUSTRIAL APPLICABILITY]

[0037]

The quaternary salt of dialkylaminoalkyl (meth)acrylate produced by the method of the present invention is widely used for a starting monomer for the production of an improving agent of fiber dyeing properties, an antistatic agent for plastics, a pigment dispersing agents or a ultraviolet curing aid in paints, a textile treating agent, a resin for toner, a coating material, a lubricant, a paper strengthening agent, adhesives, an ion exchange resin and a cationic polymeric coagulant; and the like.

CLAIMS

1. A process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate in which a dialkylaminoalkyl (meth)acrylate, a gaseous quaternizing agent and water are fed to an aqueous solution of the quaternary salt of said dialkylaminoalkyl (meth)acrylate in a reactor to react said dialkylaminoalkyl (meth)acrylate and said quaternizing agent, characterized in that said quaternizing agent is continuously fed in the form of a bubble having an average diameter of 100 μm or smaller, and that a molar ratio of said quaternizing agent to be used is in the range from 1 to 1.2 based on said dialkylaminoalkyl (meth)acrylate to be used.

2. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to Claim 1,

wherein a concentration of said quaternary salt of a dialkylaminoalkyl (meth)acrylate in said aqueous solution of said quaternary salt of the dialkylaminoalkyl (meth)acrylate in said reactor is in the range from 30% to 90% by weight.

3. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to Claim 1 or 2,

wherein a pressure in said reactor is in the range from an atmospheric pressure to 1 MPaG.

4. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to any one of Claims 1 to 3,

wherein a content of an acrylic acid generated as a by-product is less than 1,000 ppm by weight.

5. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to Claim 1,

wherein said quaternizing agent is methyl chloride,

wherein said dimethylaminoethyl (meth)acrylate is a dialkylaminoalkyl (meth)acrylate,

wherein said quaternary salt of said dialkylaminoalkyl (meth)acrylate in said aqueous solution of said quaternary salt of said dialkylaminoalkyl (meth)acrylate in said reactor is a chloride,

wherein a concentration of said chloride is in the range from 60% to 85% by weight, and

wherein a molar ratio of said quaternizing agent to be used is in the range from 1 to 1.1 based on said dialkylaminoalkyl (meth)acrylate to be used.

6. The process for the production of a quaternary salt of a dialkylaminoalkyl (meth)acrylate according to Claim 1,

wherein said quaternizing agent is methyl chloride,

wherein said dimethylaminoethyl (meth)acrylate is a dialkylaminoalkyl (meth)acrylate,

wherein said average diameter of said bubble is 80 μm or smaller,

wherein said quaternary salt of said dialkylaminoalkyl (meth)acrylate in said aqueous solution of said quaternary salt of said dialkylaminoalkyl (meth)acrylate in said reactor is a chloride,

wherein a concentration of said chloride is in the range from 70% to 85% by weight,

wherein a molar ratio of said quaternizing agent to be used is in the range from 1 to 1.05 based on said dialkylaminoalkyl (meth)acrylate to be used, and

wherein a concentration of said quaternary salt of said dialkylaminoalkyl (meth)acrylate to be produced is lower than a concentration of said quaternary salt of said dialkylaminoalkyl (meth)acrylate in said reactor, and is in the range from 50% to 82% by weight.