

METHOD OF NEUTRALIZING WASTE DEVELOPING SOLUTION CONTAINING
TETRAALKYLAMMONIUM HYDROXIDE

TECHNICAL FIELD

[0001]

The present invention relates to a novel neutralization method for neutralizing a waste developing solution containing tetraalkylammonium hydroxide (hereinafter referred to as TAAH) after using TAAH as a developing solution of photoresist, in which an organic matter derived from the photoresist (hereinafter referred to as photoresist-derived organic matter) is dissolved, by using carbon dioxide gas or carbon dioxide gas containing gas (hereinafter referred to as CO₂-containing gas). Specifically, the present invention provides a neutralization method for a waste developing solution containing TAAH, allowing efficiently removing bubbles generated in a neutralization tower without accumulating in the neutralization tower when performing neutralization reaction by supplying the above waste developing solution from the top of the tower and carbon dioxide gas or CO₂-containing gas from the bottom of the tower, and countercurrently contacting TAAH with carbon dioxide gas or CO₂-containing gas in the neutralization tower.

BACKGROUND ART

[0002]

In manufacture processes of semiconductor/liquid crystal, in case of forming a pattern on a substrate such as wafer and glass, negative or positive photoresist is applied to a metallic layer formed on the substrate surface, followed by exposing it via photomask for forming the pattern, and after developing uncured portion or cured portion with a developing solution, the above metallic layer is subject to etching to form the pattern. With the increase in integration of a semiconductor and the like, it is severely restricted that impurity, especially metallic ion and the like, is contaminated in chemicals and the like used during the manufacture process of the semiconductor. Therefore, a developing solution mainly comprising TAAH, which is an alkaline fluid not containing metallic ion, is widely used in the photolithography process. Especially, recent increase in volume of manufacture of semiconductors and liquid crystals results in increased consumption of the developing solution, so that discharge of waste developing solution containing TAAH used as a developing solution is also increased.

[0003]

In the past, the above waste developing solution containing TAAH has been rendered harmless by a publicly-known effluent treatment to dispose. For the purpose of effective utilization of resources, various regenerative methods for a waste developing solution containing TAAH have been proposed, in which the above waste developing solution is collected, purified and reused. For instance, there is proposed a method including a neutralization process, wherein waste developing solution containing TAAH is concentrated to have TAAH concentration of 10 mass% or higher, followed by neutralization by an acid such as carbon dioxide gas until pH of the solution becomes 10 or less, to deposit photoresist-derived organic matter; a separation process, wherein the photoresist deposited during the neutralization process is separated; and an electrolytic process, wherein the solution obtained in the separation process is electrolyzed to generate TAAH (refer to Patent Document 1).

[0004]

However, bubbles are continuously generated in a neutralization tower during neutralization of TAAH in the tower by supplying carbon dioxide gas in the above regenerative method. Therefore, a region occupied with bubbles may be expanded from the top to the bottom of the

tower if keeping on neutralization of TAAH, so that reaction efficiency of the neutralization may be reduced and it may also become difficult to perform stable neutralization operation.

[0005]

As a conventional means of preventing bubbles from generating in a distillation column and the like, use of a defoamer such as surfactant is generally known. However, impurity contamination is severely restricted in view of reusing the neutralized TAAH solution in the manufacture process of a semiconductor, so that defoaming technology by adding a defoamer is not preferable. Consequently, a means of preventing bubbles from generating without using a defoamer is required.

[0006]

Also, as other means of preventing bubbles from generating, there is proposed a method to form a heated surface in internal spaces at the top of the tower where the bubbles are generated, and to pass the bubbles through the heated surface for defoaming (refer to Patent Document 2).

[0007]

When applying the above defoaming technology, wherein the bubbles are passed through the heated surface for

defoaming, for neutralizing developing solution containing TAAH with carbon dioxide gas, generation of bubbles can partially be prevented at the top of the tower. However, when continuously performing neutralization operation in the neutralization tower, bubbles are continuously generated in the neutralization tower. Therefore, the bubbles distant from the heated surface may stay without contacting the heated surface, and bubbles are limited to travel, resulting in blocking contact between the bubbles and the heated surface. Consequently, the bubbles and defoamed solution may partially stay adjacent to the heated surface. A problem has been confirmed that degraded TAAH causes generation of amine odor due to locally hot area since the staying bubbles and solution are continuously heated.

[Patent Document 1] Japanese Patent No. 3110513

[Patent Document 2] Japanese Unexamined Patent
Publication H08-24510

DISCLOSURE OF INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0008]

Therefore, the purpose of the present invention is to provide a method of neutralizing a waste developing

solution by countercurrently contacting a waste developing solution containing TAAH with carbon dioxide gas or CO₂-containing gas, capable of efficiently preventing generated bubbles from accumulating in a neutralization tower without degrading TAAH.

MEANS FOR SOLVING THE PROBLEM

[0009]

The present inventors have been dedicated to studying to attain the above purpose. As a result, it was found that by drawing bubbles generated in the neutralization tower out of the tower as a bubble flow, passing the flow through a heated body outside the tower for defoaming, and returning the defoamed solution into the neutralization tower for continuing neutralization operation, the bubbles can efficiently be prevented from staying in the tower; that the above bubble flow can be contacted with a heated surface in a short time to secure defoaming treatment; and that TAAH can be cyclically used without degrading in the neutralization tower, which results in completing the present invention.

[0010]

Namely, the present invention provides a method of neutralizing a waste developing solution containing TAAH

wherein a foamed waste developing solution are defoamed by drawing bubbles out of a neutralization tower, in which the bubbles are generated in a gas-phase region at the top of the tower when neutralizing the waste developing solution by countercurrently contacting with carbon dioxide gas or CO₂-containing gas in the neutralization tower

EFFECTS OF THE INVENTION

[0011]

According to the present invention, it is possible to prevent an influence of the bubbles generated during the neutralization of the waste developing solution containing TAAH in the neutralization tower with carbon dioxide gas or CO₂-containing gas and to perform stable neutralization operation on the waste developing solution. Also, by recirculating the defoamed liquid in the neutralization tower, the loss of the liquid can efficiently be prevented.

[0012]

Further, according to the method of the present invention, in case of composing a series of processes to electrolyze carbonate generated via the neutralization and to reuse TAAH, the generated bubbles can efficiently be removed even when using CO₂-containing gas obtained in the electrolytic process as carbon dioxide gas for neutralizing

the waste developing solution containing TAAH. Therefore, it is possible to prevent carbon dioxide gas from generating in the regenerative method of the waste developing solution containing TAAH, which contributes to protection of the global environment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1 is a schematic view showing a preferable neutralization method of the present invention.

BEST MODE FOR WORKING THE INVENTION

[0014]

(Waste Developing Solution Containing TAAH)

Waste developing solution containing TAAH in which photoresist-derived organic matter is dissolved, used in the present invention (hereinafter simply referred to as waste developing solution containing TAAH) will be described in detail. A specific example of TAAH may include tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide. Among the above TAAH, tetramethylammonium hydroxide can be preferably used since it is widely used as a developing solution in semiconductor

manufacture process.

[0015]

TAAH concentration in the waste developing solution containing TAAH used in the neutralization method of the present invention is not particularly limited, and it is possible to use waste developing solution having various TAAH concentrations. TAAH concentration in the waste developing solution discharged during the semiconductor manufacture process is normally around 1% or less. For a purpose to perform an industrially efficient regeneration of the waste developing solution containing TAAH and to reduce transportation costs of the waste developing solution, it is preferable to concentrate the waste developing solution containing TAAH for increasing content rate of TAAH. When TAAH concentration in the waste developing solution containing TAAH is too low, disposal costs including transportation costs as mentioned above may be increased, and when it is too high, disposal costs for concentration procedure become high, so that TAAH concentration in the waste developing solution containing TAAH is preferably 10 to 30 mass%.

[0016]

pH of the waste developing solution containing TAAH, in which content rate of TAAH is increased by the above

concentration procedure and the like, is in a range of 13 to 15, generally in a range of 14 to 14.7.

[0017]

In the above waste developing solution containing TAAH, photoresist-derived organic matter is also dissolved.

A concentration of the above photoresist-derived organic matter differs depending on amount of dissolution of the photoresist-derived organic matter after development and solubility of the photoresist-derived organic matter in the TAAH concentration after the above-mentioned concentration procedure. For example, the concentration of the photoresist-derived organic matter dissolved in the above waste developing solution containing TAAH discharged in semiconductor manufacture process is tens to several hundred of ppm or so in terms of COD in the waste developing solution containing TAAH. As described above, when increasing the content rate of TAAH by the concentration procedure and the like, the photoresist-derived organic matter is also concentrated. Therefore, the concentration of the photoresist-derived organic matter dissolved in the waste developing solution containing TAAH, in which TAAH concentration is 10 to 30 mass%, is normally several thousand to 10000 ppm or so in terms of COD.

[0018]

As a result of studying a cause of generating bubbles during the neutralization of the waste developing solution containing TAAH with carbon dioxide gas or CO₂-containing gas, it has been found that the photoresist-derived organic matter deposited due to the neutralization reaction is one cause of foam formation. Consequently, when increasing the photoresist-derived organic matter, an amount of foam formation tends to increase, which can efficiently be eliminated in the defoaming method of the present invention as well.

[0019]

(Carbon Dioxide Gas or CO₂-Containing Gas)

In the neutralization method of the present invention, the waste developing solution containing TAAH is neutralized with carbon dioxide gas or CO₂-containing gas. As carbon dioxide gas or CO₂-containing gas used in the present invention, any industrially-available carbon dioxide gas or CO₂-containing gas can be used without any limitation. Further, CO₂-containing gas diluted by a gas which does not contribute to the neutralization reaction (hereinafter referred to as an inert gas) and the like can be used as well. When using the CO₂-containing gas diluted by the inert gas and the like, the amount of foam formation tends to increase, but the neutralization method of the

present invention, in which the bubbles are drawn out of the tower for defoaming, allows defoam operation regardless of increase in the amount of foam formation. Also, in the electrolytic process after the neutralization reaction in the present invention, carbonate and/or bicarbonate are electrolyzed, resulting in an electrolyzed gas as by-product. The electrolyzed gas varies depending on electrolytic conditions, but is CO₂-containing gas including approximately 20% of oxygen, which can preferably be used in the present invention because of the above reason. It is also preferable, in view of recycling carbon dioxide gas, to use the above electrolyzed gas as CO₂-containing gas for the neutralization reaction.

[0020]

(Neutralization Method in Neutralization Tower)

In the present invention, the neutralization tower is used as a neutralizing equipment for neutralizing the above waste developing solution containing TAAH with carbon dioxide gas or CO₂-containing gas, in which the waste developing solution containing TAAH is circulated from the top to the bottom of the tower while carbon dioxide gas or CO₂-containing gas is supplied from the bottom of the tower, allowing neutralization by contacting TAAH with carbon dioxide gas or CO₂-containing gas by countercurrent

operation. The neutralization tower is preferable as a neutralizing equipment since it enables to continuously provide the waste developing solution containing TAAH as well as carbon dioxide gas or CO₂-containing gas for performing the neutralization reaction when using the neutralization tower. FIG. 1 is a schematic view showing the most preferable neutralization method of the present invention.

[0021]

The above waste developing solution containing TAAH is supplied into a reaction tank 1 via supply piping 2 for waste developing solution containing TAAH. When supplying the waste developing solution containing TAAH above the gas-liquid interface, the waste developing solution may be discharged out of the system with bubbles generated in the upper region, and therefore, it is preferable to provide the waste developing solution directly into a reaction liquid in the neutralization tower. Carbon dioxide gas or CO₂-containing gas is supplied via supply piping 8 for carbon dioxide gas or CO₂-containing gas, moves to the top of the tower, and contacts with the waste developing solution containing TAAH for proceeding the neutralization reaction by countercurrent operation. After the neutralization reaction, the neutralized liquid is

discharged by a pump 9 through discharge piping 10 for the neutralized liquid and supplied to the subsequent process.

[0022]

The bubbles generated during the neutralization reaction move upwards in the neutralization tower, gather near the gas-liquid interface, and are discharged out of the neutralization tower from supply piping 3 for bubble flow for defoaming by a defoaming device 4. Defoaming by the defoaming device results in a solution, so that the defoamed solution may be resupplied by circulation piping 7 for defoamed liquid into the neutralization tower. By recirculating the defoamed solution in the neutralization tower, the waste developing solution containing TAAH can be efficiently utilized. Also, unreacted carbon dioxide gas or an inert gas in the CO₂-containing gas, etc., is discharged out of the system via supply piping 6 for carbon dioxide gas or CO₂-containing gas.

[0023]

When using the above neutralization tower for the neutralization reaction, the waste developing solution containing TAAH, circulating from the top to the bottom of the tower, is stirred by carbon dioxide gas supplied from the bottom of the tower. At this time, channeling and back mixing due to the drift of carbon dioxide gas may occur, so

that carbon dioxide gas is not uniformly dispersed in the neutralization tower, resulting in a portion with higher concentration of carbon dioxide gas. Since pH of the waste developing solution becomes low in the portion with higher concentration of carbon dioxide gas in the neutralization tower, a part of the photoresist-derived organic matter may be deposited in a highly-adhesive state and attach to the neutralization tower and the piping, resulting in blocking.

Therefore, it is preferable to use a multistage neutralization tower divided by trays 11 and to circulate the waste developing solution containing TAAH via down comer 12 for the purpose of accelerating uniform dispersion of carbon dioxide gas. Further preferably, filler is loaded in the neutralization tower. As the filler, any known filler used for gas-liquid reaction can be used without any limitation.

[0024]

(Neutralization Reaction)

Temperature of the above neutralization reaction is preferably 0°C to 80°C, especially preferably 20°C to 70°C, considering that the waste developing solution containing TAAH is an aqueous solution and that too high temperature may cause to deposit or to solidify photoresist in the waste developing solution containing TAAH resulting in

lowering the reaction efficiency with carbon dioxide gas. At this time, reaction liquid temperature near the gas-liquid interface at the top of the neutralization tower is 40°C or so, and temperature of the bubbles may be comparative with the above reaction liquid temperature. Also, temperature in the middle to the bottom of the neutralization tower, where the neutralization reaction is most active, is approximately 60°C to 80°C.

[0025]

Further, an end-point of the above neutralization reaction is not particularly limited, and can be properly set in view of durability of a filtration film used in the subsequent partition process of the photoresist-derived organic matter, an influence of pH of the waste developing solution in the electrolytic process, etc. in the regenerative method of the waste developing solution. The above end-point of the neutralization reaction may be preferably set normally within a range of pH 8 to 13.5.

[0026]

(Supply Method of Carbon Dioxide Gas)

In the present invention, carbon dioxide gas or CO₂-containing gas is supplied from the bottom of the tower. A supply method of the carbon dioxide gas or CO₂-containing gas is not particularly limited, and any known supply

method can be applied without any limitation. The known supply methods of the carbon dioxide gas or CO₂-containing gas may include, for instance, a supply method by piping with a gas supply port, a supply method by a line mixer and a supply method by an ejector. In general, when supplying carbon dioxide gas by the line mixer or ejector, the supplied carbon dioxide gas becomes bubbles having small bubble diameter, resulting in increase in contact area between the carbon dioxide gas and waste developing solution containing TAAH. Therefore, these methods are preferable since reaction efficiency with the waste developing solution containing TAAH is improved.

[0027]

Also, when using the CO₂-containing gas, this includes the above inert gas in addition to carbon dioxide gas, and the inert gas foams in the gas-liquid interface and is discharged. When using line mixer, ejector and the like in the supply method for the above CO₂-containing gas, bubbles with small bubble diameter and high liquid ratio are generated in the gas-liquid interface at the top of the tower, so that defoaming rate tends to lower. Therefore, when using the CO₂-containing gas including the above electrolyzed gas, the supply method by piping with gas supply port is most preferable since it allows the

generation of bubbles with large bubble diameter, which is easy to eliminate.

[0028]

In the above supply method by piping with the gas supply port, a diameter of the gas supply port may be properly determined in view of a size of the neutralization tower, reaction efficiency of the above neutralization reaction, defoamability of the defoaming device and the like. When the bubble diameter is too small, bubbles with high liquid ratio may be generated, resulting in low defoaming effect. Too large bubble diameter may cause to reduce the contact area of the CO₂-containing gas and waste developing solution containing TAAH, so that reaction efficiency of the neutralization reaction is lowered and excessive CO₂-containing gas is required to terminate the neutralization reaction. Therefore, the bubble diameter of the CO₂-containing gas supplied into the neutralization tower is preferably 2 mm to 6 mm as a bubble diameter nearest to the gas supply port. A shape of the above gas supply port is not particularly limited as long as the port can supply the CO₂-containing gas with the above bubble diameter, and a circular form is preferable since the bubbles are orbicular, and maintenance such as cleaning of the piping is easy. The bubble diameter of the supplied

gas can be controlled by an area of the gas supply port, and the area of the gas supply port is in a range of preferably 0.07 to 80 mm², further preferably 3 to 30 mm². The above area corresponds to a circle having the diameter of 0.3 to 10 mm, preferably 2 to 6 mm.

[0029]

Further, the above gas supply port is preferably 1 or more in the piping, further preferably 1 to 15, in view of efficiently performing the neutralization reaction. A total area of the gas supply port in the piping having the above number of the gas supply ports is normally 20 to 300 mm² or so per 100 L, a volume of the reaction tank.

[0030]

(Defoaming)

The bubbles generated in the neutralization reaction between the waste developing solution containing TAAH and the carbon dioxide gas or CO₂-containing gas in the present invention move upwards in the neutralization tower, gather near the gas-liquid interface, and are discharged out of the neutralization tower as a bubble flow from the supply piping 3 for bubble flow for defoaming by the defoaming device 4. The defoamed solution is resupplied into the neutralization tower via the circulating piping 7 for defoamed liquid.

[0031]

As a discharge method of the above bubble flow, any known discharge method can be used without any limitation. The known discharge methods may include a discharge method by suction of the bubble flow using a suction pump, a discharge method in which unreacted carbon dioxide gas or the inert gas in the CO₂-containing gas is used to discharge out of the neutralization tower, etc. Among these, the discharge method in which unreacted carbon dioxide gas or the inert gas in the CO₂-containing gas is used to discharge out of the neutralization tower is preferable since it is simple in systems and economical.

[0032]

As a defoaming method of the bubbles discharged out of the neutralization tower as a bubble flow in the above discharge method, any known defoaming method can be used without any limitation as long as it is a defoaming method without using a defoamer. The known defoaming methods may include a defoaming method by blow of impeller and the like, a defoaming method by spraying droplets, a defoaming method by irradiating ultrasonic on the surface of the liquid and a defoaming method by contacting with heated body 5. Among the above defoaming methods, the defoaming method by contacting with the heated body is most

preferable in view of defoaming efficiency.

[0033]

In a contact method between the bubbles discharged out of the neutralization tower and the heated body in the above defoaming method, using a multitubular heat exchanger such as a double pipe-type heat exchanger, a liquid including the bubbles drawn out of the neutralization tower is circulated in the pipes and the heated body is circulated outside of the pipes, so that the bubbles drawn out of the neutralization tower can be contacted with the heated body. The bubbles drawn out of the neutralization tower is contacted with the heated body through the pipe wall and the liquid including the bubbles is defoamed. After defoaming, the defoamed liquid may be resupplied into the neutralization tower and reused for the neutralization reaction as a waste developing solution containing TAAH.

[0034]

A temperature of the above heated body used for defoaming the bubble flow including the bubbles is higher than the temperature of the discharged bubbles, preferably 70°C or more, further preferably 80°C or more. At 70°C or less, the bubble flow can be defoamed by contacting for a long time, but it is not industrially efficient since the large and complicated defoaming device is required to

contact for a long time. Therefore, the temperature of the heated body is preferably 70°C or more, particularly preferably 80°C or more in view of defoaming efficiency. Also, higher temperature of the heated body may improve defoaming rate, but TAAH tends to be degraded to generate amine odor depending on the contact time when contacting with the high-temperature heated body. Therefore, the temperature of the heated body is preferably 80°C or more and below the temperature for degrading TAAH, and is preferably 80°C to 110°C, most preferably 80°C to 97°C in view of the defoaming rate and prevention of TAAH degradation. The heated body at 80 to 97°C can be obtained by using industrial-level hot water as a medium. Note that long heating results in defoaming effect with low temperature of the heated body. Also, when the temperature of the heated body is high, it is possible to prevent TAAH degradation and to obtain defoaming effect by shortening the contact time with the heated body.

[0035]

The contact time of the bubble flow and the heated body in the present invention may vary depending on a shape of the bubbles included in the bubble flow and liquid ratio of the bubbles, and is therefore hardly generalized, but it may be properly determined depending on a medium of the

heated body and the temperature as well as the above-mentioned shape of the bubbles and the liquid ratio of the bubbles. The longer contact time allows to securely defoam. However, the longer contact time indicates longer defoaming time, which is not industrially efficient, and further tends to generate amine odor caused by the degraded TAAH. Therefore, the contact time of the bubble flow and the above heated body at 80 to 97°C is preferably 1 to 30 seconds, particularly preferably 3 to 15 seconds.

[0036]

In case that a heated body at 80 to 97°C is used as the heated body and contact time is 1 to 30 seconds, defoaming ability of the defoaming device is 1 to 6 m³/h·m² in terms of unit area of the contact surface with the heated body.

[0037]

(Subsequent Process of Neutralizing Process)

The TAAH in the waste developing solution containing TAAH becomes carbonate and bicarbonate by the neutralization method of the present invention, resulting in lowering a ratio of TAAH in which the photoresist-derived organic matter can be dissolved. Then, the photoresist-derived organic matter becomes less soluble in the waste developing solution to deposit the photoresist-

derived organic matter. The deposited organic matter can be removed by any known operation such as filtration. Further, filtrate including the above carbonate and bicarbonate of TAAH is electrolyzed to obtain TAAH. At this time, the above-mentioned electrolyzed gas is generated as by-product, the electrolyzed gas can be cyclically used as CO₂-containing gas in the neutralization method of the present invention as described above. Note that the dissolved metallic ions and the like can also be removed by ion-exchange resin, chelate resin and the like after filtration of the photoresist-derived organic matter.

EXAMPLE

[0038]

Hereinafter, the present invention will be further specifically described showing the following Examples, but the present invention is not limited to these Examples.

[0039]

Example 1

A neutralization tower made from clear vinyl chloride was used for neutralization. The size of the neutralization tower was 210 mm in diameter and 2500 mm in height, and 3 trays having down comer were placed inside.

[0040]

Further, a polypropylene-filler (HEILEX manufactured by Toyo Tire & Rubber Co., Ltd, 3/4 inch) was filled in the hollow portion. Also, a nozzle was placed on the side at a height of 1850 mm from the bottom of the tower to make an opening for drawing out bubbles. CO₂-containing gas was supplied from a supply pipe having 5 gas supply ports with a diameter of 2 mm (cross-sectional area of 3 mm²).

[0041]

As a waste developing solution containing TAAH, a waste developing solution containing tetramethylammonium hydroxide (hereinafter referred to as TMAH) at pH 14.7 with a concentration of 20 mass% was used.

[0042]

First, the neutralization tower was filled with 56 L of the above waste developing solution containing TMAH, and CO₂-containing gas (carbon dioxide gas with a concentration of 75 vol%) was supplied from the bottom at a rate of 520 L/h under standard conditions to start a neutralization reaction. Then, the above waste developing solution containing TMAH was supplied at a rate of 10 L/h from supply piping for waste developing solution containing TAAH, for performing neutralization reaction by countercurrent operation.

[0043]

Bubbles generated due to the neutralization reaction was drawn out from the above nozzle, and let through to contact with a double pipe-type heat exchanger (manufactured by SUS, 20 mm in diameter, 750 L, 0.04 m² in heat transfer area) having a heated body with a temperature of 90°C for a contact time of 7 seconds. As a result, 90% or more of the bubbles were eliminated, and the remaining 10% or less of the bubbles formed an intermittent phase having a void, which indicated the defoaming effect. The defoaming ability was 3.3 m³/h·m². No amine odor, attributed to the degraded TMAH, was recognized at this time.

[0044]

Examples 2 to 10

Except for changing the temperature of the heated body of the heat exchanger and the contact time to conditions shown in Table 1, the neutralization reaction was performed as in Example 1. The results are shown in Table 1. Note that the defoaming effect was evaluated with a ratio of the remaining bubbles after passing through the heat exchanger with respect to the bubbles supplied to the heat exchanger, i.e. a residual ratio of the bubbles after passing through the heat exchanger. No amine odor, attributed to the degraded TMAH, was recognized in Examples 1 to 9 as well.

In Example 10, defoaming effect was good while faint amine odor was recognized.

[Table 1]

Table 1

Example	Heated Body Temp. (°C)	Contact Time (sec)	Defoaming Effect*	Amine Odor
1	90	7	A	No
2	95	7	A	No
3	80	7	B	No
4	90	11	A	No
5	80	11	A	No
6	90	4	A	No
7	80	4	B	No
8	70	7	C	No
9	110	3	C	No
10	110	11	A	Yes

* Residual ratio of the bubbles

A: 10% or less, B: 10% to 30%, C: 30% to 70%

[0045]

Examples 11 to 12

Except for changing the diameter of the gas supply port of the supply pipe for CO₂-containing gas and the number of the gas supply ports to those shown in Table 2, the neutralization reaction was performed as in Example 1. The results are shown in Table 2. Note that the defoaming effect was evaluated as in the above Table 1. No amine odor, attributed to the degraded TMAH, was recognized in both examples as well.

[Table 2]

Table 2

Example	Gas Supply Port Diameter (mm)	No. of Gas Supply Ports	Defoaming Effect	Amine Odor
11	2	10	A	No
12	5	4	A	No

[0046]

Examples 13 to 16

Except for changing the diameter of the neutralization tower, the diameter of the gas supply port of the supply pipe for CO₂-containing gas, the number of the gas supply port, and the supply rate of the CO₂-containing gas to those shown in Table 3, neutralization reaction was performed as in Example 1. The results are shown in Table 3. Note that the defoaming effect was evaluated as in the above Table 1. No amine odor, attributed to the degraded TMAH, was recognized in any examples as well.

[Table 3]

Table 3

Example	Tower Dia. (mm)	Gas Supply Port Dia. (mm)	No. of Gas Supply Ports	Gas Supply Rate (L/h)	Contact Time (sec)	Defoaming Effect	Amine Odor
13	80	1	2	60	7	A	No
14	80	1	10	60	7	A	No
15	300	5	7	1000	7	A	No
16	300	10	1	1000	7	A	No

[0047]

Example 17

A neutralization tower made from clear vinyl chloride was used for neutralization. The size of the neutralization tower was 210 mm in diameter and 2500 mm in height, and 3 trays having down comer were placed inside.

[0048]

Further, a polypropylene-filler (HEILEX manufactured by Toyo Tire & Rubber Co., Ltd, 3/4 inch) was filled in the hollow portion. Also, a nozzle was placed on the side at a height of 1850 mm from the bottom of the tower to make an opening for drawing out bubbles, and a double pipe-type heat exchanger (manufactured by SUS, 20 mm in diameter, 750 L, 0.04 m^2 in heat transfer area) having a heated body with a temperature of 90°C was placed. Further, circulating piping for defoamed liquid was placed for circulating the liquid passing through the heat exchanger into the neutralization tower, and connected to the side at a height of 1750 mm from the bottom of the neutralization tower. CO_2 -containing gas was supplied from a supply pipe having 5 ports with a diameter of 2 mm.

[0049]

As a waste developing solution containing TAAH, a waste developing solution containing tetramethylammonium hydroxide (hereinafter referred to as TMAH) at pH 14.7 with a concentration of 20 mass% was used.

[0050]

First, the neutralization tower was filled with 56 L of the above waste developing solution containing TMAH (the height was 1800 mm at this time.), and CO₂-containing gas (carbon dioxide gas with a concentration of 75 vol%) was supplied from the bottom at a rate of 520 L/h under standard conditions to start a neutralization reaction. Then, the above waste developing solution containing TMAH was supplied at a rate of 10 L/h from supply piping for waste developing solution containing TAAH for performing the neutralization reaction by countercurrent operation.

[0051]

At the start of the neutralization reaction, a foam formation layer with a height of 50 to 100 mm was generated in the gas-phase region above the gas-liquid interface, but the generated bubbles became a bubble flow with unreacted carbon dioxide gas and inert gas in the CO₂-containing gas to introduce to the heat exchanger. 90% or more of the bubbles disappeared and the defoamed liquid was circulated in the neutralization tower. The contact time of the bubbles with the heat exchanger was 7 seconds.

[0052]

As a result of continuous neutralization reaction under the above conditions, the foam formation layer showed

no growth even after 1 month and it was possible to continue the neutralization reaction. No amine odor, attributed to the degraded TMAH, was recognized as well.

[0053]

Comparative Example 1

A neutralization tower made from clear vinyl chloride was used for neutralization. The size of the neutralization tower was 210 mm in diameter and 2500 mm in height, and 3 trays having down comer were placed inside.

[0054]

Further, a polypropylene-filler (HEILEX manufactured by Toyo Tire & Rubber Co., Ltd, 3/4 inch) was filled in the hollow portion. CO₂-containing gas was supplied from a supply pipe having 5 ports with a diameter of 2 mm.

[0055]

As a waste developing solution containing TAAH, a waste developing solution containing tetramethylammonium hydroxide (hereinafter referred to as TMAH) at pH 14.7 with a concentration of 20 mass% was used.

[0056]

First, the neutralization tower was filled with 56 L of the above waste developing solution containing TMAH, and CO₂-containing gas (carbon dioxide gas with a concentration of 75 vol%) was supplied from the bottom at a rate of 520

L/h under standard conditions to start a neutralization reaction. Then, the above waste developing solution containing TMAH was supplied at a rate of 10 L/h from supply piping for waste developing solution containing TAAH for performing the neutralization reaction by countercurrent operation.

[0057]

At the start of the neutralization reaction, a foam formation was observed near the gas-liquid interface, and therefore, the supply of the waste developing solution containing TMAH and CO₂-containing gas were temporarily stopped, and the region above the interface was heated at 90°C. As a result, the foam formation disappeared. Then, while heating the upper region of the neutralization tower at 90°C, the supply of the waste developing solution containing TMAH and CO₂-containing gas was restarted to continue the neutralization reaction. As a result, an amount of the formed bubbles remained in the gas-liquid interface increased as the neutralization reaction proceeded, and the bubble layer finally grew to the top of the neutralization tower, so that the neutralization reaction was stopped. At this time, amine odor, attributed to the degraded TMAH, was recognized in the neutralization tower.

[0058]

Comparative Example 2

Except for changing the temperature of the heated body to 80°C, and supplying the CO₂-containing gas at 315 L/h under standard conditions, neutralization reaction was performed as in Comparative Example 1. An amount of the formed bubbles remained in the gas-liquid interface was increased as the neutralization reaction proceeded, and the bubble layer finally grew to the top of the neutralization tower, so that the neutralization reaction was stopped. At this time, weak amine odor, attributed to the degraded TMAH, was recognized in the neutralization tower.

CLAIMS

1. A method of neutralizing waste developing solution containing tetraalkylammonium hydroxide comprising steps of
countercurrently contacting waste developing solution containing tetraalkylammonium hydroxide with carbon dioxide gas or carbon dioxide gas containing gas in a neutralization tower, the waste developing solution including dissolved photoresist-derived organic matter in addition to the tetraalkylammonium hydroxide, and
defoaming a foamed waste developing solution by drawing bubbles out of the neutralization tower, in which the bubbles are generated in a gas-phase region at the top of the tower during the neutralization of the waste developing solution.
2. The method of neutralizing as set forth in claim 1, wherein the bubble drawn from the neutralization tower is contacted with a heated body for defoaming.
3. The method of neutralizing as set forth in claim 2, wherein a temperature of the heated body is 80 to 97°C, and contact time between the heated body and a liquid composing the bubble is 1 to 30 seconds.

4. The method of neutralizing as set forth in any one of claims 1 to 3, wherein the carbon dioxide gas containing gas is obtained by electrolyzing carbonate and/or bicarbonate after said neutralization.

5. The method of neutralizing as set forth in any one of claims 1 to 4, wherein

the carbon dioxide gas containing gas is supplied from piping having a gas supply port equipped at the bottom of the neutralization tower,

1 or more gas supply ports are supplied in the piping, and

an area of each gas supply port is in a range of 0.07 to 80 mm².

6. The method of neutralizing as set forth in claim 1, further comprising a step of resupplying the defoamed solution into the neutralization tower.