

METHOD OF NEUTRALIZING WASTE DEVELOPING SOLUTION CONTAINING
TETRAALKYLAMMONIUM HYDROXIDE

TECHNICAL FIELD

[0001]

The present invention relates to a novel neutralization method for neutralizing 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. Specifically, the present invention relates to a neutralization method, capable of preventing blocking due to deposition of photoresist-derived organic matter in a reaction tank when neutralizing waste developing solution containing TAAH, and capable of effectively removing photoresist included in the waste developing solution because of high filterability of the photoresist-derived organic matter deposited at neutralization.

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-mentioned 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 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

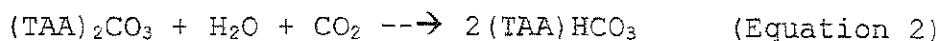
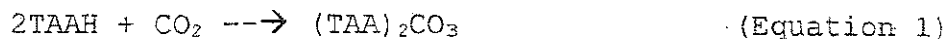
effective utilization of resources, a regenerative method for a waste developing solution containing TAAH has been proposed, in which TAAH is collected from the above waste developing solution, purified and reused. For instance, there is proposed a method including a neutralization process, wherein spent TAAH aqueous solution, in which TAAH concentration is concentrated to 10 mass% or higher, is neutralized to have pH of 10 or less by an acid such as carbon dioxide gas and photoresist-derived organic matter is deposited; a separation process, wherein the photoresist-derived organic matter 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]

In the neutralization of the waste developing solution containing TAAH by carbon dioxide gas, as shown in the following equations 1 and 2, carbonate and bicarbonate of TAAH are generated to lower the ratio of TAAH for dissolving the photoresist-derived organic matter. Then, the photoresist-derived organic matter in the waste developing solution becomes less soluble and is deposited, so that it is possible to remove the deposit by operation

such as filtration.

[Chemical Equation 1]



[0005]

The above regenerative method can remove photoresist-derived organic matter, i.e. major impurity, by easy operation such as filtration. Especially in case of using carbon dioxide gas as an acid for neutralization, incorporated impurities such as metallic ion, which becomes a problem in the manufacture process of semiconductor, are lowered, so that this regenerative method of waste developing solution containing TAAH is industrially favorable.

[Patent Document 1] Japanese Patent No. 3110513

DISCLOSURE OF INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0006]

However, in the neutralization process of waste developing solution containing TAAH by carbon dioxide gas to deposit photoresist-derived organic matter as an impurity, when neutralizing simply by injecting carbon dioxide gas into the waste developing solution, the

deposited photoresist-derived organic matter is highly adhesive, and adheres to an inner wall of the reaction tank or inside of piping connecting thereto, often causing these to block. Also, as another problem, filterability in the removing process is extremely deteriorated and operating efficiency is lowered since the above deposited photoresist-derived organic matter is particulate. In addition, TAAH is dangerous since it is strongly-alkaline and highly lipid soluble, so that increase in washing treatment of the blocked piping becomes a problems for operation.

MEANS FOR SOLVING THE PROBLEM

[0007]

The present inventors have further studied to attain the above purpose. As a result, the following were found in case of neutralization by adding carbon dioxide gas to a waste developing solution containing tetraalkylammonium hydroxide with pH of 13 or more, in which photoresist-derived organic matter is dissolved: (1) photoresist-derived organic matter starts deposition when the above waste developing solution has pH of around 13, and deposition is completed for the most part when the solution is further neutralized to have pH of around 11.5, and (2)

deposition of the photoresist-derived organic matter is especially remarkable when pH of the above waste developing solution is within a range of between 13 and 12. Consequently, it was found that it is possible to form a floc with large particle size and to obtain the deposited photoresist-derived organic matter having extremely high filterability when an amount of carbon dioxide gas added to neutralize the above waste developing solution with pH of the above specified range is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution with pH of 13. Also, it was confirmed that the photoresist-derived organic matter is deposited in a fashion similar to recrystallization in this operation, resulting in high removal efficiency for the organic matter. In addition, the inventors surprisingly found that the above deposit has low adhesion, so that it is possible to prevent blocking of the piping and the like in a most effective way, and came to complete the present invention based on the findings.

[0008]

In a first aspect, the present disclosure is a method of neutralizing waste developing solution containing tetraalkylammonium hydroxide comprising steps of:

adding carbon dioxide gas to a waste developing

solution containing tetraalkylammonium hydroxide with pH of 13 or more, in which a photoresist-derived organic matter is dissolved, and

neutralizing the waste developing solution containing tetraalkylammonium hydroxide until pH becomes 11.5 or less, wherein:

an amount of carbon dioxide gas, added to said waste developing solution while pH thereof changes from 13 to 12, is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution when pH thereof is 13.

[0009]

In a second aspect, the present disclosure is a method of neutralizing waste developing solution containing tetraalkylammonium hydroxide comprising steps of:

adding carbon dioxide gas to a waste developing solution containing tetraalkylammonium hydroxide with pH of over 13.7, in which a photoresist-derived organic matter is dissolved, and

neutralizing the waste developing solution containing tetraalkylammonium hydroxide until pH becomes 11.5 or less, wherein:

a first neutralization, in which pH of the waste developing solution becomes any pH within a range of 13 or

more to 13.7 or less, and a second neutralization after obtaining pH within the range are performed in separate reaction tanks, and

in the second neutralization, an amount of carbon dioxide gas, added to said waste developing solution while pH thereof changes from 13 to 12, is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution when pH thereof is 13.

In a third aspect, there is provided a method of neutralizing waste developing solution containing tetraalkylammonium hydroxide comprising steps of: adding carbon dioxide gas to a waste developing solution containing tetraalkylammonium hydroxide with pH of over 13.7, in which a photoresist-derived organic matter is dissolved, and neutralizing the waste developing solution containing tetraalkylammonium hydroxide until pH becomes 11.5 or less, wherein: a rate of adding carbon dioxide gas is changed between a first neutralization, in which pH of the waste developing solution becomes any pH within a range of 13 to 13.7, and a second neutralization after obtaining pH within the range, in the second neutralization, an amount of carbon dioxide gas, added to said waste developing solution while pH thereof is in a range within 13 to 12, is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution when pH thereof is 13, and an amount of carbon dioxide gas added in the first neutralization per unit of time is larger than the amount of carbon dioxide gas added in the second neutralization.

EFFECTS OF THE INVENTION

[0010]

According to the neutralization method of the present invention, it is possible to form a floc with large particle size and to deposit a photoresist-derived organic matter, so that deposit having extremely high filterability can be obtained. Therefore, it is possible to efficiently remove the photoresist-derived organic matter which becomes a problem in the electrolytic process after neutralize reaction. Also, the above deposit has low adhesion and rarely adheres to piping, so that there is no blocking of the piping, etc., and it is industrially safe and efficient.

[0011]

Further, by performing the first neutralization, in

which pH of the waste developing solution becomes any pH within a range of 13 or more to 13.7 or less, and the second neutralization after obtaining pH within the range in separate reaction tanks, each of the neutralizations can be done in parallel. Consequently, it results in shortening operation time in the neutralizations, which is industrially efficient.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1 is a schematic view showing a preferable embodiment in the present invention, in which the first neutralization reaction and second neutralization reaction are performed in separate reaction tanks.

BEST MODE FOR WORKING THE INVENTION

[0013]

(Waste Developing Solution Containing TAAH with Dissolved Photoresist-derived Organic Matter)

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. In the present invention, 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.

[0014]

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 neutralization 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%.

[0015]

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.

[0016]

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. In the neutralization method of the present invention, higher concentration of the photoresist-derived organic matter, dissolved in the waste developing solution containing TAAH for neutralization reaction, results in higher removal efficiency of the organic matter, so that higher concentration is effective.

[0017]

The concentration of the photoresist-derived organic matter dissolved in the above waste developing solution

containing TAAH is tens to several hundreds of ppm or so in terms of COD in the waste developing solution containing TAAH discharged in semiconductor manufacture process for example. Also, an effective use of waste developing solution containing TAAH is recently proposed, in which a waste developing solution containing TAAH used in a development process is added with a developing solution containing TAAH to adjust TAAH concentration, and the adjusted solution is then reused in another development process. Consequently, the concentration of the photoresist-derived organic matter in the waste developing solution containing TAAH tends to be higher than the above concentration. In any waste developing solution containing TAAH, when increasing content rate of TAAH by the concentration procedure and the like as described above, 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 thousands to 10000 ppm or so in terms of COD.

[0018]

(Carbon Dioxide Gas)

In the neutralization method of the present invention,

carbon dioxide gas is added to the waste developing solution containing TAAH with pH of 13 or more to neutralize. As carbon dioxide gas used in the present invention, any industrially-available carbon dioxide gas can be used without any limitation. Also, carbon dioxide gas diluted by an inert gas and the like can be used as well. After neutralizing the waste developing solution containing TAAH by carbon dioxide gas, the generated carbonate and bicarbonate are electrolyzed, resulting in an electrolyzed gas as by-product in addition to generation of TAAH. The electrolyzed gas mainly includes carbon dioxide gas, and the electrolyzed gas can be used as reused carbon dioxide gas for neutralization reaction.

[0019]

(Amount of Carbon Dioxide Gas)

It is most characteristic in the present invention that an amount of carbon dioxide gas, added to said waste developing solution while pH thereof changes from 13 to 12, is controlled to 0.15 L/hr (hereinafter a volume of carbon dioxide gas indicates the volume in standard conditions) or less, more preferably 0.10 L/hr or less, per 1 mole of TAAH in the waste developing solution when pH thereof is 13 in a method of neutralizing waste developing solution containing TAAH in which the waste developing solution containing TAAH

with pH of 13 or more is added with carbon dioxide gas to neutralize until pH becomes 11.5 or less. As described above, the photoresist-derived organic matter is remarkably deposited while pH of the above waste developing solution changes from 13 to 12. Therefore, by controlling the amount of carbon dioxide gas in the above pH range, it is possible to control deposition rate of the photoresist-derived organic matter and to obtain deposit having high filterability.

[0020]

The smaller the amount of the above carbon dioxide gas, controlling effects of deposition rate of the photoresist-derived organic matter become high, but too small amount causes longer neutralization time. Consequently, in view of industrial efficiency, the amount is preferably 0.05 L/hr or more, more preferably 0.01 L/hr or more.

[0021]

Also, most of the photoresist-derived organic matter deposits before pH become 11.5. Therefore, it is more preferable for obtaining deposit having high filterability that the amount of carbon dioxide gas when pH of the waste developing solution changes from 13 to 11.5 is controlled in the above range.

[0022]

It is not preferable that the amount of carbon dioxide gas in the above range exceeds 0.15 L/hr per 1 mole of TAAH in the waste developing solution at pH13 since controlling effects of the deposition rate of the photoresist-derived organic matter is low, and the deposited photoresist-derived organic matter may have high adhesion or may be particulate. On the other hand, when the amount of carbon dioxide gas is too low, time for neutralization reaction becomes long. Therefore, in view of industrial efficiency and the like, the amount of the above carbon dioxide gas may be properly determined based on time for changing pH from 13 to 12 or 11.5. Normally, it is preferable to properly determine the amount of carbon dioxide gas so that time for changing pH from 13 to 12 is 0.8 to 10 hours, preferably 2.0 to 10 hours, or time for changing pH of the above waste developing solution from 13 to 11.5 is 3 to 30 hours, preferably 5.0 to 30 hours.

[0023]

Time point to start adding the above amount of carbon dioxide gas (hereinafter referred to as a starting point of controlling addition of carbon dioxide gas) may be any time until pH of the above waste developing solution containing TAAH becomes 13, and may be properly determined in view of

equipments for neutralization reaction, processing capacity and the like. For example, the starting point of controlling addition of carbon dioxide gas can be set, in terms of factor of safety, when pH is above 13. Also, the amount of carbon dioxide gas can be the above-identified amount in the entire pH range from starting neutralization to termination, reaction time for neutralization reaction becomes long, which cannot be industrially efficient. Therefore, in the waste developing solution containing TAAH with pH of over 13.7, it is especially preferable to properly set the starting point of controlling addition of carbon dioxide gas at any time when pH is within the range of 13 to 13.7.

[0024]

(Method of Providing Carbon Dioxide Gas)

As a method of adding carbon dioxide gas in the above amount, any known method of supplying carbon dioxide gas can be employed. For example, there may be mentioned a method of intermittently supplying carbon dioxide gas, a method of continuously supplying a specific amount of carbon dioxide gas and the like.

[0025]

Among the above methods of adding carbon dioxide gas, the method of continuously supplying a specific amount of

carbon dioxide gas is preferable because of easy process control and simple reaction equipments.

[0026]

(Neutralization up to Starting Point of Controlling Addition of Carbon Dioxide Gas)

For the neutralization up to the above starting point of controlling addition of carbon dioxide gas (hereinafter referred to as first neutralization) in the present invention, reaction conditions and the like may be properly determined in view of equipments for the neutralization reaction, processing capacity, etc. As described above, the amount of carbon dioxide gas in the first neutralization can be same as the amount of the neutralization after the starting point of controlling addition of carbon dioxide gas (hereinafter referred to as second neutralization), but reaction time for neutralization reaction becomes long, indicating that it is not industrially efficient. Therefore, the amount of carbon dioxide gas in the first neutralization is preferably larger than the amount in the second neutralization.

[0027]

However, depending on the conditions, channeling or back mixing may occur due to drift of the supplied carbon

dioxide gas, so that carbon dioxide gas is not uniformly dispersed in the reaction tank, 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, a part of the photoresist-derived organic matter may be deposited in a highly-adhesive state until the above starting point of controlling addition of carbon dioxide gas and attached to piping and the like, resulting in blocking. Therefore, it is further preferable that the amount of carbon dioxide gas in the above first neutralization is 1.0 L/hr or less, preferably 0.7 L/hr or less, per 1 mole of tetraalkylammonium hydroxide in the waste developing solution prior to the neutralization.

[0028]

Also, the smaller amount of carbon dioxide gas causes higher anti-deposition effect of the photoresist-derived organic matter in the first neutralization, but too small amount results in longer neutralization time. It is therefore preferable that the amount is 0.1 L/hr or more in view of industrial efficiency.

[0029]

(End-point of Neutralization)

An end-point of neutralization of the waste developing

solution containing TAAH by carbon dioxide gas in the neutralization method of the present invention can be properly set in view of the following conditions when the waste developing solution has pH of 11.5 or less after neutralization process: durability of a filtration film used in a partition process of the photoresist-derived organic matter, an influence of pH of the waste developing solution in the electrolytic process, etc. The above end-point of the neutralization may be properly set normally within a range of pH 8 to 11.5. Also, as for neutralization of the waste developing solution with pH of less than 11.5, the reaction conditions and the like may be properly determined in view of equipments for the neutralization reaction and processing capacity.

[0030]

Especially, most of the photoresist-derived organic matter deposit before pH becomes 12 to 11.5 in the neutralization method of the present invention. Therefore, it is especially preferable to properly set the end-point of neutralization within the pH range of 11 to 11.5. It is especially preferable to set the end-point of neutralization within the above range because of the following points in addition to the above reason: neutralization time can be shortened, excess of carbon

dioxide gas is needed for accelerating neutralization because of lowered reaction efficiency of carbon dioxide gas used for neutralization of carbonate of TAAH at pH of less than 11.5; in the electrolytic process, higher rate of carbonate in the waste developing solution available for electrolysis causes higher power efficiency since 2 moles of TAAH are generated in electrolysis of 1 mole of carbonate while 1 mole of TAAH is generated per 1 mole of bicarbonate; etc.

[0031]

(System for Neutralization Method)

As described above, as for system for the neutralization method in the present invention, there may be mentioned a neutralization method using a single reaction tank and a neutralization method using 2 or more multiple reaction tanks. Among these, as the neutralization method using a single reaction tank, there may be mentioned a method wherein an entire neutralization reaction is performed with carbon dioxide gas in a specific amount of 0.15 L/hr or less per 1 mole of TAAH in the waste developing solution at pH13, and a method wherein the amounts of carbon dioxide gas are changed between the above first neutralization and second neutralization. Also, as the above neutralization method using 2 or more multiple

reaction tanks, there may be mentioned a method wherein the first neutralization and the second neutralization are performed in separate reaction tanks.

[0032]

Among the above systems, the neutralization method, in which 2 or more multiple reaction tanks are used and the first neutralization and the second neutralization are performed in separate reaction tanks, is preferable since independent process control is possible in respective reaction tanks, and independent neutralization can be done in parallel to shorten operation time. Further, by performing the first neutralization and the second neutralization in separate reaction tanks, each of the neutralization can be done in a plurality of reaction tanks. However, there are problems that too many reaction tanks result in complex process control and operation on reaction in each reaction tank, and that installing of reaction tanks is expensive, etc. Therefore, it is most preferable to use one reaction tank each for the first neutralization and the second neutralization (neutralization method using 2 reaction tanks).

Hereinafter, a neutralization method of the present invention, wherein each of the first neutralization and the second neutralization is performed in a reaction tank, will

be described in detail. FIG. 1 is a schematic view showing the most preferable embodiment in the present invention wherein the first neutralization and the second neutralization are performed in separate reaction tanks.

[0033]

(First Neutralization)

In a reaction tank 1, the first neutralization is performed. Waste developing solution containing TAAH is supplied via supply piping 3 for waste developing solution containing TAAH. In the reaction tank 1, carbon dioxide gas is supplied via supply piping 4 for carbon dioxide gas for neutralization in the reaction tank 1. The neutralized liquid is discharged by a pump 5 into supply piping 6 for waste liquid from the reaction tank 1, and supplied into a reaction tank 2 via the supply piping 6. Unreacted carbon dioxide gas and the like are discharged out of the system via supply piping 7 for discharging unreacted gas.

[0034]

As described above, the amount of carbon dioxide gas in the first neutralization may be properly determined in view of equipments, processing capacity and the like for neutralization reaction. Because of industrial efficiency, the above amount is preferably larger than the amount of carbon dioxide gas in the second neutralization. Further,

in view of influences by channeling and back mixing due to drift of carbon dioxide gas in the reaction tank 1, the above amount is further preferably 1.0 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution before the neutralization.

[0035]

A pump 8 and circulation piping 9 are further placed in the reaction tank 1, and a reaction measuring device 10 is placed in the above circulation piping. As a result, reaction in the reaction tank 1 is easily controllable. As the reaction measuring device, any known measuring devices, such as an ultrasonic concentration meter, for measuring concentrations of solutes in a solution can be used as well as a pH meter since concentrations of TAAH and carbonate in the reaction tank 1 at the end-point of neutralization can be easily calculated when known concentration of the waste developing solution containing TAAH is used for the reaction.

[0036]

When bubbling in the reaction liquid becomes a problem in the above neutralization, supply piping for carbon dioxide gas can be placed in the above circulation piping to supply carbon dioxide gas into the circulation piping by supplying means such as line mixer and ejector and to

introduce the gas into the reaction tank via the circulation piping.

Temperature of the neutralization reaction in the reaction tank 1 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 reaction efficiency with carbon dioxide gas.

[0037]

Specific examples of the above reaction tank 1 may include a reaction tank having a stirring wing, packed tower in which a filler is packed to improve diffusional efficiency of carbon dioxide gas, and a neutralization tower in which the above waste developing solution containing TAAH is circulated from the top to the bottom while carbon dioxide gas is supplied from the bottom to contact TAAH with carbon dioxide gas by countercurrent operation. Among the above reaction tanks, the neutralization tower, allowing the reaction by countercurrent operation, is further preferable since it enables to continuously perform neutralization.

[0038]

As mentioned above, a neutralization method using the above neutralization tower which is a multistage column having a plurality of trays 11 is especially preferable to be used in the first neutralization since pH of the above waste developing solution is easily stabilized in each stage divided by the trays 11, and pH of the waste developing solution can be reduced in a stepwise fashion by circulating the above waste developing solution from the top to bottom through each stage.

[0039]

The tray 11 used in the above multistage column is formed from a perforated plate having a plurality of penetrated pores and a down comer 12. Said waste developing solution containing TAAH is circulated from the top to the bottom through the down comer 12, and carbon dioxide gas is circulated from the bottom to the top through the pore of the perforated plate. A circulating rate of the waste developing solution containing TAAH in the neutralization tower can be controlled by changing an internal diameter of the down comer 12. Too small internal diameter of the above down comer 12 causes longer neutralization time, which is not economical. Too large internal diameter causes lower controlling effect of the circulating rate of the above waste developing solution.

Therefore, the internal diameter of the down comer 12 may be preferably 0.1 to 0.5%, especially preferably 0.2 to 1.0% per the internal diameter of the neutralization tower.

Also, a circulating rate of carbon dioxide gas can be controlled by changing aperture ratio of the perforated plate. Too low aperture ratio causes longer neutralization time, which is not economical, while too high aperture ratio causes lower controlling effect of the circulating rate of the above carbon dioxide gas. Therefore, the aperture ratio is preferably 3 to 10%.

[0040]

Also, when the number of the trays 11 of the above multistage column is larger, i.e. the number of the divided stages is higher, controlling effect of pH becomes high. However, too many dividers cause higher production cost of the multistage column. Therefore, the number of the trays 11 is preferably 2 to 4, i.e. the number of the stages for circulating the above waste developing solution is preferably 3 to 5.

[0041]

Further, for the purpose of accelerating uniform diffusion of carbon dioxide gas, it is especially preferable to load the filler into each stage divided by trays 11. As the filler, any known filler used for gas-

liquid reaction can be used without any limitation.

[0042]

(Second Neutralization)

After the first neutralization in the reaction tank 1, the second neutralization is performed in the reaction tank 2. The waste developing solution neutralized in the reaction tank 1 (hereinafter referred to as waste liquid from reaction tank 1) is supplied to the reaction tank 2 via the supply piping 6 for waste liquid from the reaction tank 1. After supplying the waste liquid from reaction tank 1 to the reaction tank 2, carbon dioxide gas is supplied via supply piping 13 for carbon dioxide gas for neutralization. After neutralization, the reaction liquid is discharged by a pump 14 via supply piping 15 for neutralized solution for partition process to separate photoresist. Unreacted carbon dioxide gas and the like are discharged out of the system via piping 16 for discharging unreacted gas.

[0043]

In the second neutralization, the amount of carbon dioxide gas while pH of the above waste developing solution changes from the starting pH, at the starting point of controlling addition of carbon dioxide gas, to 12 or 11.5 is 0.15 L/hr or less per 1 mole of TAAH in the waste

developing solution when pH thereof is 13.

[0044]

For the purpose of improving stirring efficiency of the reaction liquid, circulation piping 18 can be placed in the reaction tank 2 to react the solution in the reaction tank 2 while circulating with the pump 17. When bubbling in the reaction liquid becomes a problem, supply piping for carbon dioxide gas can be placed in the above circulation piping to supply carbon dioxide gas into the circulation piping by a supplying means such as line mixer and ejector and to introduce the gas into the reaction tank via the circulation piping.

[0045]

In addition, by placing reaction measuring device 19 in the above circulation piping, reaction in the reaction tank 2 is controllable. As the reaction measuring device, any known measuring devices, such as an ultrasonic concentration meter, for measuring concentrations of solutes in a solution can be used as well as a pH meter since concentrations of carbonate and bicarbonate at pH of the end-point of neutralization can be easily calculated when concentrations of carbonate and TAAH is known in the waste liquid from reaction tank 1 supplied into the reaction tank 2.

[0046]

(Method for Removing Deposited Photoresist)

In the neutralization method of the present invention, deposited photoresist-derived organic matter is large floc and has low adhesion, resulting in high filterability. A method for removing the photoresist-derived organic matter in the partition process includes decantation, centrifugation, filter press, filtration by ultrafiltration film and the like, and any known solid-liquid separation equipments can be used. Also, the photoresist-derived organic matter deposited in the neutralization method of the present invention can directly be used for solid-liquid separation since it has the above characteristics. It is also possible to add a filter aid to the deposited organic matter for further improving filtration efficiency and to mix prior to solid-liquid separation. The filter aid used for the solid-liquid separation includes activated carbon, diatomaceous earth, cellulose and the like. Among these, it is preferable to use the filter aid such as activated carbon and diatomaceous earth because they are industrially available at a moderate price.

EXAMPLE

[0047]

The method of the present invention will be further specifically described based on the following Examples, but the present invention is not limited to these Examples.

[0048]

Example 1

A neutralization system produced with clear vinyl chloride having formation shown in FIG. 1 was used. The size of the reaction tank 1 was 100 mm in diameter and 1000 mm in height, and 3 trays having down comer were placed inside. The size of the reaction tank 2 was 250 mm in diameter and 800 mm in height.

[0049]

Further, as waste developing solution containing TAAH, waste developing solution containing tetramethylammonium hydroxide (hereinafter referred to as TMAH) at pH 14.7 was used. Note that TMAH concentration in the waste developing solution was 20 mass%, and content of the photoresist-derived organic matter was 5000 ppm in terms of COD.

[0050]

First, the reaction tank 1 was filled with 6 L of waste developing solution containing TAAH, and carbon dioxide gas was supplied at 17.3 L/hr from supply piping 4 for carbon dioxide gas at the bottom of the reaction tank 1 to neutralize until pH became 13. Then, while supplying

carbon dioxide gas at 17.3 L/hr, the above waste developing solution was supplied at 4.6 L/hr from supply piping 3 for waste developing solution containing TAAH at the top of the reaction tank 1, for continuously neutralizing by the countercurrent operation. When sampling the waste liquid from reaction tank 1 discharged from the supply piping 6 of the waste liquid from reaction tank 1 for checking pH, pH was 13. The amount of carbon dioxide gas in the reaction tank 1 at pH13 was 0.39 L/hr in standard conditions per 1 mole of TMAH in the waste developing solution before neutralization (hereinafter the amount of carbon dioxide gas indicates a volume in standard conditions). It was observed that no photoresist-derived organic matter was deposited in the reaction tank 1 in the above neutralization.

[0051]

Next, the reaction tank 2 was filled with 20 L of the neutralized liquid from the reaction tank 1, and then, carbon dioxide gas was supplied for neutralization from the supply piping 4 for carbon dioxide gas at the bottom of the reaction tank 2 so as to have the amount of carbon dioxide gas of 0.01 L/hr per 1 mole of TMAH when pH of the waste developing solution was 13, so that the reaction liquid at pH11.5 was obtained. Time required for changing pH of the

waste developing solution from 13 to 12 was 9.7 hours, and time required for changing pH from 13 to 11.5 was 28.5 hours.

[0052]

The reaction liquid was added with "Shirasagi" (product name of activated carbon distributed by Japan EnviroChemicals, Ltd.) as filter aid at a rate of 1.0 wt%. After stirring, a membrane filter H100 A142C (product name, by Advantec Toyo Kaisha, Ltd., pore diameter 1 μ m) was set in a press filter KST-142-UH (product name, by Advantec Toyo Kaisha, Ltd., diameter 142 mm), and pressure filtration was performed at 0.15 MPa. The filtration was well performed to obtain clarified filtrate. COD of the filtrate was 60 ppm. Also, the processing speed for filtrating the above reaction liquid was 500 L/m³·hr, calculated from the filtration rate.

[0053]

Examples 2 to 6

Except for changing neutralization conditions in the reaction tank 1, i.e. supply rate of waste developing solution, supply rate of carbon dioxide gas and the amount of carbon dioxide gas per 1 mole of TMAH in the waste developing solution before neutralization, to those shown in Table 1, and changing neutralization condition in the

reaction tank 2, i.e. the amount of carbon dioxide gas per 1 mole of TMAH when pH of the waste developing solution was 13, to those shown in Table 1, neutralization reaction was performed as in Example 1. Table 1 shows time required for changing pH of the waste developing solution in the reaction tank 2 from 13 to 12 and 11.5, and filtration results after neutralization.

[Table 1]

Table 1

EXAMPLE	Reaction Tank 1			Reaction Tank 2			Filtration	
	WDS Supply Rate (L/hr)	CO ₂ Supply Rate (L/hr)	CO ₂ Amount ^{*1} (L/hr)	CO ₂ Amount ^{*2} (L/hr)	Time to pH12 ^{*3} (hr)	Time to pH11.5 ^{*3} (hr)	Filtration Capacity (L/m ³ ·hr)	COD of Filtrate (ppm)
2	0.2	0.9	0.02	0.01	9.7	28.5	500	60
3	4.6	17.3	0.39	0.03	4.9	14.3	500	60
4	4.6	17.3	0.39	0.13	1.0	2.9	300	70
5	2.3	8.7	0.20	0.03	4.9	14.3	500	60
6	4.6	17.3	0.39	0.02	6.0	17.6	500	60

NOTE: WDS=Waste Developing Solution; CO₂=Carbon Dioxide Gas*1: Amount of CO₂ per 1 mole of TMAH in the waste developing solution before neutralization in standard conditions*2: Amount of CO₂ per 1 mole of TMAH at pH13 in the waste developing solution in standard conditions

*3: Time required to change to change pH in the waste developing solution from 13 to 12 or 11.5

[0054]

Example 7

Using the same neutralization system as in Example 1, the reaction tank 1 was first filled with 6 L of the same waste developing solution containing TAAH as in Example 1, and carbon dioxide gas was supplied at 24.8 L/hr from supply piping 4 for carbon dioxide gas at the bottom of the reaction tank 1 to neutralize until pH became 13.5. Then, while supplying carbon dioxide gas at 24.8 L/hr, the above waste developing solution was supplied at 7.5 L/hr from supply piping 3 for waste developing solution containing TAAH at the top of the reaction tank 1, for continuously neutralizing by the countercurrent operation. When sampling the waste liquid from reaction tank 1 discharged from supply piping 6 for waste liquid from reaction tank 1 for checking pH, pH was 13.5. The amount of carbon dioxide gas in the reaction tank 1 at pH13.5 was 0.57 L/hr in standard conditions per 1 mole of TMAH in the waste developing solution before neutralization. It was observed that no photoresist-derived organic matter was deposited in the reaction tank 1 in the above neutralization.

[0055]

Next, the reaction tank 2 was filled with 20 L of the

neutralized liquid from the reaction tank 1, and then, carbon dioxide gas was supplied for neutralization from the supply piping 4 for carbon dioxide gas at the bottom of the reaction tank 2 so as to have the amount of carbon dioxide gas of 0.07 L/hr per 1 mole of TMAH when pH of the waste developing solution was 13, so that the reaction liquid at pH11.5 was obtained. Time required for changing pH of the waste developing solution from 13 to 12 was 2.8 hours, and time required for changing pH from 13 to 11.5 was 6.3 hours.

[0056]

The reaction liquid was filtered as in Example 1. The filtration was well performed to obtain clarified filtrate.

COD of the filtrate was 60 ppm. Also, the processing speed for filtrating the above reaction liquid was 400 L/m³·hr, calculated from the filtration rate.

[0057]

Example 8

Except for using waste developing solution containing TMAH including 8000 ppm of the photoresist-derived organic matter in terms of COD at pH14.7, neutralization reaction was performed as in Example 7. Note that TMAH concentration in the waste developing solution was 20 mass%.

[0058]

The reaction liquid was filtered as in Example 7. The filtration was well performed to obtain clarified filtrate.

COD of the filtrate was 90 ppm. Also, the processing speed for filtrating the above reaction liquid was 400 L/m³·hr, calculated from the filtration rate.

[0059]

Example 9

Using the same waste developing solution containing TAAH as in Example 1, neutralization reaction in the reaction tank 1 was performed as in Example 6.

[0060]

Next, the reaction tank 2 was filled with 20 L of the neutralized liquid from the reaction tank 1, and then, carbon dioxide gas was supplied for neutralization from the supply piping 4 for carbon dioxide gas at the bottom of the reaction tank 2 so as to have the amount of carbon dioxide gas of 0.02 L/hr per 1 mole of TMAH when pH of the waste developing solution was 13. The neutralized liquid from the reaction tank 1 at pH13 was neutralized until pH became 12, followed by increasing supply rate of carbon dioxide gas to 0.50 L/hr, and the neutralization was further performed until pH of the reaction liquid became 11.5. Time required for changing pH of the waste developing

solution from 13 to 12 was 6.0 hours, and time required for changing pH from 13 to 11.5 was 6.5 hours.

[0061]

The reaction liquid was filtered as in Example 1. The filtration was well performed to obtain clarified filtrate.

COD of the filtrate was 70 ppm. Also, the processing speed for filtrating the above reaction liquid was 350 L/m³·hr, calculated from the filtration rate.

[0062]

Comparative Examples 1 to 2

Except for changing neutralization conditions in the reaction tank 1, i.e. supply rate of waste developing solution, supply rate of carbon dioxide gas and the amount of carbon dioxide gas per 1 mole of TMAH in the waste developing solution before neutralization, to those shown in Table 2, and also changing neutralization condition in the reaction tank 2, i.e. the amount of carbon dioxide gas per 1 mole of TMAH when pH of the waste developing solution is 13, to those shown in Table 2, neutralization reaction was performed as in Example 1. Table 2 shows time required for changing pH of the waste developing solution in the reaction tank 2 from 13 to 12 and 11.5, and filtration results after neutralization. Note that filtration in Comparative Example 2 was not completed since the press

filter had blocking during the filtration. Therefore, it was impossible to calculate the processing speed for filtration.

[Table 2]

Table 2

COMP. EXAMPLE	Reaction Tank 1			Reaction Tank 2			Filtration	
	WDS Supply Rate (L/hr)	CO ₂ Supply Rate (L/hr)	CO ₂ Amount ^{*1} (L/hr)	CO ₂ Amount ^{*2} (L/hr)	Time to pH12 ^{*3} (hr)	Time to pH11.5 ^{*3} (hr)	Filtration Capacity (L/m ³ .hr)	COD of Filtrate (ppm)
1	2.3	8.7	0.20	0.21	0.6	1.8	100	70
2	4.6	17.3	0.39	0.27	0.5	1.4	—	60

NOTE: COMP.=COMPARATIVE; WDS=Waste Developing Solution; CO₂=Carbon Dioxide Gas

*1: Amount of CO₂ per 1 mole of TMAH in the waste developing solution before neutralization in standard conditions

*2: Amount of CO₂ per 1 mole of TMAH at pH13 in the waste developing solution in standard conditions

*3: Time required to change to change pH in the waste developing solution from 13 to 12 or 11.5

CLAIMS

1. A method of neutralizing waste developing solution containing tetraalkylammonium hydroxide comprising steps of:

adding carbon dioxide gas to a waste developing solution containing tetraalkylammonium hydroxide with pH of 13 or more, in which a photoresist-derived organic matter is dissolved, and

neutralizing the waste developing solution containing tetraalkylammonium hydroxide until pH becomes 11.5 or less, wherein:

an amount of carbon dioxide gas, added to said waste developing solution while pH thereof changes from 13 to 12, is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution when pH thereof is 13.

2. The method of neutralizing waste developing solution containing tetraalkylammonium hydroxide as set forth in claim 1, wherein time required for changing pH of the waste developing solution from 13 to 12 is 0.8 to 10 hours.

3. The method of neutralizing waste developing solution

containing tetraalkylammonium hydroxide as set forth in claim 1, wherein an amount of carbon dioxide gas, added to the waste developing solution when pH thereof changes from 13 to 11.5, is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution when pH thereof is 13.

4. The method of neutralizing waste developing solution containing tetraalkylammonium hydroxide as set forth in claim 3, wherein time required for changing pH of the waste developing solution from 13 to 11.5 is 3 to 30 hours.

5. A method of neutralizing waste developing solution containing tetraalkylammonium hydroxide comprising steps of:

adding carbon dioxide gas to a waste developing solution containing tetraalkylammonium hydroxide with pH of over 13.7, in which a photoresist-derived organic matter is dissolved, and

neutralizing the waste developing solution containing tetraalkylammonium hydroxide until pH becomes 11.5 or less, wherein:

a first neutralization, in which pH of the waste developing solution becomes any pH within a range of 13 or

more to 13.7 or less, and a second neutralization after obtaining pH within the range are performed in separate reaction tanks, and

in the second neutralization, an amount of carbon dioxide gas, added to said waste developing solution while pH thereof changes from 13 to 12, is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution when pH thereof is 13.

6. The method of neutralizing waste developing solution containing tetraalkylammonium hydroxide as set forth in claim 5, wherein an amount of carbon dioxide gas per unit of time in the first neutralization is larger than the amount of carbon dioxide gas in the second neutralization.

7. The method of neutralizing waste developing solution containing tetraalkylammonium hydroxide as set forth in claim 6, wherein the amount of carbon dioxide gas in the first neutralization is 1.0 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution before neutralization.

8. The method of neutralizing waste developing solution containing tetraalkylammonium hydroxide as set forth in

claim 5, wherein the first neutralization is performed in a multistage neutralization column.

9. A method of neutralizing waste developing solution containing tetraalkylammonium hydroxide comprising steps of:

adding carbon dioxide gas to a waste developing solution containing tetraalkylammonium hydroxide with pH of over 13.7, in which a photoresist-derived organic matter is dissolved, and

neutralizing the waste developing solution containing tetraalkylammonium hydroxide until pH becomes 11.5 or less, wherein:

a rate of adding carbon dioxide gas is changed between a first neutralization, in which pH of the waste developing solution becomes any pH within a range of 13 to 13.7, and a second neutralization after obtaining pH within the range,

in the second neutralization, an amount of carbon dioxide gas, added to said waste developing solution while pH thereof is in a range within 13 to 12, is controlled to 0.15 L/hr or less per 1 mole of tetraalkylammonium hydroxide in the waste developing solution when pH thereof is 13, and

an amount of carbon dioxide gas added in the first

neutralization per unit of time is larger than the amount of carbon dioxide gas added in the second neutralization.

10. The method of neutralizing waste developing solution containing tetraalkylammonium hydroxide as set forth in any one of claims 5 to 9, wherein a concentration of tetraalkylammonium hydroxide in the waste developing solution containing tetraalkylammonium hydroxide prior to the first neutralization is 10 to 30 mass%.

METHOD OF NEUTRALIZING WASTE DEVELOPING SOLUTION CONTAINING
TETRAALKYLAMMONIUM HYDROXIDE

ABSTRACT OF THE DISCLOSURE

A method of neutralizing a developer waste liquid containing a tetraalkylammonium hydroxide wherein an organic matter derived from photoresist is dissolved through reaction with carbon dioxide gas, in which clogging by intra-column resist precipitation at neutralization can be effectively prevented and in which resist precipitated at neutralization ensures a high filterability and can be effectively removed. The method of neutralizing a developer waste liquid containing a tetraalkylammonium hydroxide comprises adding carbon dioxide gas to a developer waste liquid containing tetraalkylammonium hydroxide of 13 or higher pH value in which an organic matter derived from photoresist is dissolved to thereby carry out neutralization to a pH value of 11.5 or below, wherein the rate of carbon dioxide gas added from the time at which the pH of the developer waste liquid is 13 to the time at which the pH reaches 12 is 0.15 L/hr or less per mol of tetraalkylammonium hydroxide contained in the developer waste liquid at the time of pH 13.