

(Title of the Invention)

METHOD OF TREATING WASTE DEVELOPING SOLUTION

(Technical Field)

5 The present invention relates to a method of
treating a waste developing solution recovered from a
photoresist-developing step in a process for producing
electronic parts such as semiconductor devices (LSIs),
liquid crystal displays (LCDs), printed boards and the
like. More specifically, the invention relates to a
10 method of treating a waste developing solution capable
of refining a used tetraalkylammonium hydroxide
aqueous solution (waste developing solution) recovered
from the photoresist-developing step developing
maintaining stability for extended periods of time and
15 of utilizing the refined solution again as the
developing solution.

(Background Art)

In a process for producing electronic parts such
as semiconductor devices, liquid crystal displays,
20 printed boards and the like, there exists a step in
which a film of a negative or positive photoresist is
formed on a substrate such as a wafer, the photoresist
film is irradiated with light of a predetermined
pattern through a mask and, then, the unnecessary
25 photoresist is dissolved by using a developing
solution. After the developing, the surface of the
substrate of a portion from where the photoresist has
been removed is etched by using an etching solution
thereby to form, for example, a predetermined circuit
30 pattern on the surface of the substrate. When
developed relying upon the alkali dissolution, there
is in many cases used a tetraalkylammonium hydroxide
(TAA hydroxide) aqueous solution as the developing
solution.

35 When the above developing is conducted, the

photoresist is usually dissolved in the used TAA hydroxide aqueous solution (i.e., dissolved in the waste developing solution) discharged from the step of developing. In order to enhance the utilization
5 factor of the developing solution in recent years, a method has been employed according to which the waste developing solution is passed through a membrane such as a nanofilter, and the solution that has passed therethrough is treated through a precision filter to
10 remove solid components such as particles and is circulated into the step of developing (see patent document 1).

Attempts have also been made to refine the waste developing solution which is the used TAA hydroxide
15 aqueous solution to utilize it again (see patent document 2). As the refining method, there has been known a method of regenerating the TAA hydroxide aqueous solution by neutralizing the waste developing solution to precipitate the photoresist, removing the
20 precipitated photoresist, and electrolyzing the obtained TAA salt to use it as the developing solution.

According to the method of the above patent document 1, however, the used TAA hydroxide aqueous
25 solution which is to be used again for the step of developing has a low purity, exhibits deteriorated developing characteristics, and cannot be used for the step of developing for forming precise and fine wiring layers, but can simply be used for the step of
30 developing that does not require precision. Therefore, the waste developing solution is not circulated to the step of developing that requires precision but is simply used again in the step of developing that does not require precision.

35 According to the patent document 2, on the other

hand, the purity is not recovered to a sufficient degree despite of the refining treatment by electrolysis, often developing troubles in the refining apparatus such as an electrolyzer and making it difficult to continue the operation for extended periods of time. Concretely speaking, when the refining treatment is conducted by electrolysis, the ion-exchange membrane in the electrolyzer is deteriorated making it difficult to recover the used TAA hydroxide aqueous solution that is to be treated to a sufficient degree and, besides, the voltage of the electrolyzer is elevated hindering the stable operation from continuing for extended periods of time.

Patent document 1: JP-A-2002-361249

Patent document 2: Japanese Patent No. 3110513
(Disclosure of the Invention)

It is therefore an object of the present invention to provide a method of treating a waste developing solution, which is capable of refining, for extended periods of time maintaining stability, the waste developing solution containing TAA hydroxide discharged from a photoresist-developing step and, as a result, regenerating a TAA hydroxide aqueous solution of a high purity that can be used again as the developing solution even for the photoresist-developing step that requires a high degree of precision.

The present inventors have conducted a keen study in order to solve the above technical problem. As a result, the inventors have discovered a new fact that trace amounts of metal impurities accumulate after the repetitive use in the step of developing and seriously affect the refining which is based on the electrolysis and, upon changing the process for treating the waste

developing solution depending upon the amounts of metal impurities, the TAA hydroxide aqueous solution of a high purity can be regenerated maintaining stability for extended periods of time, and have
5 arrived at the present invention.

According to the present invention, there is provided a method of treating a waste developing solution recovered from a photoresist-developing step where a tetraalkylammonium hydroxide aqueous solution
10 is used as a developing solution, comprising:

measuring a concentration of a tetraalkylammonium and contents of metal impurities in the waste developing solution;

when the contents of the metal impurities are all
15 not more than 50 ppm per the tetraalkylammonium, refining the waste developing solution to regenerate the tetraalkylammonium hydroxide solution so as to be used as the developing solution; and

when the content of at least one kind of metal
20 impurity is more than 50 ppm per the tetraalkylammonium, disposing the waste developing solution or diluting the waste developing solution with the unused tetraalkylammonium hydroxide aqueous solution which is the developing solution so that the
25 content of the metal impurity that was more than 50 ppm becomes not more than 50 ppm, and refining the waste developing solution that is diluted to regenerate the tetraalkylammonium hydroxide aqueous solution so as to be used as the developing solution.

30 In treating the waste developing solution containing tetraalkylammonium hydroxide (TAA hydroxide) recovered from the photoresist-developing step according to the present invention, a distinguished feature resides in the provision of a
35 step (inspection step) for measuring the contents of

various kinds of metal impurities, and a process for treating the waste developing solution is changed depending upon the contents of metal impurities per the TAA measured at the inspection step.

5 That is, when the content of metal impurities per the TAA is not more than a predetermined value (50 ppm), the waste developing solution is refined to regenerate the TAA hydroxide aqueous solution making it possible to conduct the refining treatment
10 maintaining stability for extended periods of time. Further, the TAA hydroxide aqueous solution that is regenerated is highly pure and can be used again as a developing solution even for the photoresist-

15 When the content of metal impurities is more than the predetermined value (50 ppm) per the TAA, the waste developing solution is disposed of or is diluted with the highly pure tetraalkylammonium hydroxide aqueous solution so that the content of the metal
20 impurities becomes smaller than the predetermined value. The diluted solution is refined to regenerate the TAA hydroxide aqueous solution. In this case, too, the refining treatment can be conducted
25 Further, the TAA hydroxide aqueous solution that is regenerated can be used again as a developing solution even for the photoresist-developing step that requires a high precision.

30 The waste developing solution containing large amounts of metal impurities can be disposed of by feeding it to a particular portion of the facility for producing a cement maintaining safety and efficiency without involving such work as treating the waste water.

35 (Brief Description of the Drawings)

Fig. 1 is a flowchart of a method of treating a waste developing solution according to the invention;

Fig. 2 is a flowchart illustrating the steps of refining in the method of treating the waste

5 developing solution according to the invention; and

Fig. 3 is a flowchart illustrating the steps of producing a highly pure tetraalkylammonium hydroxide aqueous solution used in the treating method of the invention.

10 (Best Mode for Carrying Out the Invention)

Referring to Fig. 1, in the method of treating a waste developing solution of the present invention, a waste developing solution 2 discharged from a developing step 1 and is recovered, is fed to an inspection step 4 through a concentration step 3, and is fed to a refining step 5, to a disposal step 6 or to a refining step 7 by dilution depending upon the content of metal impurities in the waste developing solution inspected at the inspection step 4. The developing solution regenerated at the refining step 5 or at the refining step 7 by dilution, is circulated to the developing step 1 and is used again.

(Developing step 1)

25 In the present invention, the developing step 1 is a photoresist-developing step employed in a process for producing various electronic parts such as semiconductor devices, liquid crystal displays and printed boards and is, particularly, a step of developing a photoresist that uses a TAA hydroxide aqueous solution as a developing solution.

30 Concrete examples of the TAA hydroxide used for the developing solution include tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, methyltriethylammonium hydroxide,

trimethylethylammonium hydroxide,
dimethyldiethylammonium hydroxide, trimethyl(2-
hydroxyethyl)ammonium hydroxide, triethyl(2-
hydroxyethyl)ammonium hydroxide, dimethyldi(2-
5 hydroxyethyl)ammonium hydroxide, diethyldi(2-
hydroxyethyl)ammonium hydroxide, methyltri(2-
hydroxyethyl)ammonium hydroxide, ethyltri(2-
hydroxyethyl)ammonium hydroxide and tetra(2-
10 hydroxyethyl)ammonium hydroxide. The concentration of
the TAA hydroxide in the developing solution is,
usually, about 1 to about 5% by mass though it may
vary depending upon the kind of the TAA hydroxide.

The developing solution is used for removing
excess of photoresist (photoresist of portions not
15 irradiated with light) from the photoresist layer
applied onto the surface of the substrate of a metal
material forming, for example, a wiring layer.
(Waste developing solution 2)

The waste developing solution 2 discharged from
20 the developing step 1 contains the photoresist
dissolved in the developing solution and a metal which
is a substrate material together with the TAA
hydroxide. In the present invention, the waste
developing solution 2 is passed through a nanofilter
25 or is treated through a precision filter to remove the
solid components such as the photoresist and
particles, and is used again through the following
steps.

The developing waste solution (used TAA hydroxide
30 aqueous solution) that is recovered contains the
photoresist dissolved therein, surfactant components
stemming from the photoresist and organic impurities
such as organic solvent components, as well as metal
impurities such as Al and Cu stemming from the metal
35 wiring material on the surface of the substrate, Fe,

Cr and Ni stemming from the container for containing the developing solution or the pipe material (for example, SUS used for supplying and recovering the developing solution), and Na stemming from the surfactant. In particular, though it may vary depending upon the degree of contamination in the factory and the systems, the contents of metal impurities are in a range of 500 ppb to 100 ppm per the tetraalkylammonium (TAA) in the waste developing solution. Among them, the contents of Al and Cu are very greater than the contents of other metal impurities. If the above waste developing solution 2 is simply put to the refining treatment, the refining systems such as electrolyzing facility and dialyzing facility are damaged within short periods of time and the purity of the refined TAA hydroxide aqueous solution (regenerated developing solution) decreases. As described already, these problems become conspicuous with an increase in the amount of the metal impurities. According to the present invention, therefore, the waste developing solution 2 is subjected to the refining after the inspection step 4 that will be described later.

(Concentration step 3)

Prior to putting the waste developing solution 2 to the inspection step 4, the solution is, first, concentrated through the concentration step 3 to increase the concentration of TAA in the waste developing solution 2. That is, as described earlier, the concentration of the TAA hydroxide in the developing solution used in the developing step 1 is 1 to 5% by mass. Therefore, the TAA concentration in the waste developing solution recovered from the developing step 1 is, usually, about several percent.

The waste developing solution 2 containing the TAA

(TAA hydroxide) at such a concentration tends to be foamed very easily. In transferring the waste developing solution 2 to the refining step, therefore, the foaming often causes such troubles in the pipe as dispersion in the flow rate and defective filling in the tank to which the waste developing solution is to be transferred. According to the present invention, the waste developing solution 2 is concentrated; e.g., the TAA concentration in the waste solution is increased to be not lower than 10% by mass and, preferably, about 15 to about 25% by mass to effectively prevent inconvenience caused by the foaming. Further, the concentration decreases the burden on transferring the waste developing solution 2.

There is no particular limitation on the method of concentration and, generally, the concentration is effected by using a thin-film evaporator which is little affected by the foaming.

(Inspection step 4)

In the present invention, it is necessary to put the waste developing solution 2 concentrated as described above to the inspection step 4 to measure the concentration of the tetraalkylammonium (TAA) and contents of various kinds of metal impurities in the waste developing solution 2, and to select the step of treatment to be subsequently conducted depending upon the content of metal impurities per the TAA.

That is, according to the present invention, a reference value of the contents of metal impurities per the TAA is set to be 50 ppm, and the waste developing solution 2 is fed to the refining step 5 that will be described later when the contents of various kinds of metal impurities are measured to be all not more than the above reference value, and is

fed to the waste disposal step 6 or to the refining step 7 by dilution when the content of any kind of metal impurities exceeds the above reference value. Thus, upon selecting the subsequent step of treatment depending upon the content of the metal impurities, it is allowed to efficiently avoid adverse effects (deterioration of the ion-exchange resin and of the ion-exchange membrane, elevation of voltage in the electrolyzer) on the refining step 5 caused by metal impurities, to conduct the refining treatment maintaining stability for extended periods of time and to regenerate the TAA hydroxide aqueous solution of a high purity.

In the present invention, further, when the waste developing solution 2 is to be fed to the refining step 5, it is desired that the contents of metal impurities are not more than the reference value and that the total amount thereof is not larger than 120 ppm and, particularly, not larger than 100 ppm per the TAA. That is, even when the total amount of various kinds of metal impurities is too great, the refining step 5 is adversely affected to a large extent by the metal impurities. Therefore, when the total amount of metal impurities exceeds the above range, it is desired to feed the waste developing solution to the disposal step 6 or to the refining step 7 by dilution.

In the present invention in principle, metal impurities of all kinds contained in the waste developing solution 2 should be measured for their contents. As described earlier, however, the contents of Al, Cu and Na are very larger than the contents of other metal impurities. Therefore, other metal impurities (e.g., Fe, Cr, Ni, etc.) may be not measured but metal impurities of three kinds only, i.e., Al, Cu and Na, may be measured for their

contents to control the method based on the above-mentioned reference value making it possible to decrease the work of inspection.

When the total content of organic impurities per the TAA is measured at the inspection step 4 to be too great (e.g., not smaller than 2% by mass and, particularly, not smaller than 5% by mass per the TAA) and when the waste developing solution 2 is to be fed to the refining step 5, it is desired that the waste developing solution 2 is diluted with the unused TAA hydroxide aqueous solution which is the developing solution and, particularly, with the highly pure TAA hydroxide aqueous solution that will be described later to adjust the total content of organic impurities to be smaller than the above range. As described earlier, the organic impurities stem from the photoresist, from the surfactant components contained in the photoresist and from the organic solvent components. A decrease in the total content of the organic impurities works to decrease a burden at the refining step 5 effectively suppressing the wear of electrodes and elevation of voltage in the electrolyzer, and enhancing the treating efficiency.

In the above inspection step 4, the contents of various components are measured by a known method by sampling the waste developing solution 2. For example, the TAA concentration can be measured by a potentiometric titration method, the contents of various kinds of metal impurities can be measured by using an inductive coupling plasma mass analyzer (ICP-MS), and the total content of organic impurities can be calculated by a method of oxygen consumption by using potassium permanganate (JIS K 0101) conducted at 100°C or by measuring the absorbency by using an absorptiometer.

(Refining step 5)

When the content of metal impurities is smaller than the above reference value in the present invention, the waste developing solution 2 is fed to the refining step 5 so as to be refined. The refining treatment includes a neutralizing/separating step 11 and an electrolyzing step 13 as illustrated in Fig. 2.

In the neutralizing/separating step 11, the TAA hydroxide contained in the waste developing solution 2 is neutralized to form a tetraalkylammonium salt (TAA salt) thereby to precipitate the photoresist that is dissolved in the waste developing solution 2. The precipitated photoresist is, then, separated to obtain a TAA salt aqueous solution 15. Though there is no particular limitation on the acidic substance used for neutralizing the TAA hydroxide, there is usually used hydrochloric acid or carbonic acid gas.

There is no particular limitation, either, on the means for separating the precipitated photoresist, and filtration is usually preferably used. In this case, it is desired to use, as a filtering assistant, activated carbon, cellulose or diatomaceous earth from the standpoint of removing fine solid particles (organic impurities and metal impurities) other than the photoresist that is precipitated. In order to remove metal impurities, further, the solution after filtered may be brought into contact with the ion-exchange resin.

The TAA salt aqueous solution 15 obtained through the neutralizing/separating step 11 is, then, subjected to the electrolysis at an electrolyzing step 13. Through the electrolysis, the TAA hydroxide is formed from the TAA salt, and the refined TAA hydroxide aqueous solution is obtained, i.e., regenerated developing solution 17 is obtained.

The TAA salt is electrolyzed by using an electrolyzer equipped with an anode chamber and a cathode chamber partitioned by a cation-exchange membrane. That is, by conducting the electrolysis by feeding the TAA salt aqueous solution to the anode chamber, the TAA ions formed in the anode chamber transmits through the ion-exchange membrane and migrate into the cathode chamber, and a highly pure TAA hydroxide aqueous solution is obtained from the cathode chamber. Known electrolyzing conditions can be employed without any particular limitation.

Prior to the electrolyzing step 13, it is desired that the TAA concentration in the TAA salt aqueous solution 15 is concentrated to be not lower than 20% by mass and, particularly, to be 25 to 30% by mass by using a thin-film evaporator from the standpoint of enhancing the efficiency of the electrolysis. That is, when the TAA concentration is low, the electrolysis can be executed but the operation of the electrolyzer may become complex due to the balance with the water. Therefore, a high concentration is desired even from the standpoint of electrolytic efficiency.

(Disposal step 6)

In the waste disposal step 6 that is effected for the waste developing solution 2 containing metal impurities in amounts in excess of the above reference value (50 ppm per the TAA), the waste developing solution is disposed of by an ordinary burning treatment. It is desired that the disposal treatment is conducted by using a burning facility in which there exists a region having a temperature of not lower than 400°C, desirably, not lower than 600°C and, more desirably, not lower than 800°C and by throwing the waste developing solution 2 into the above

temperature region. By throwing the waste developing solution 2 into the above temperature region, it is presumed that the TAA burns generating heat in large amounts as it is decomposed after the water is
5 instantaneously evaporated. As a result, the temperature is not greatly lowered at the portion where the waste developing solution is thrown and, besides, depending upon the cases, the amount of heat can be supplied to a degree that requires the fuel in
10 decreased amounts in the burning facility. Besides, offensive odor components can be almost all eliminated in the exhaust gas.

The disposal treatment can be favorably conducted by utilizing, for example, a cement firing facility or
15 a facility for firing dolomite and calcined lime. Particularly desirably, the disposal treatment can be conducted by utilizing a cement firing facility comprising a rotary kiln equipped with a pre-heater. The cement firing facility has a region of a
20 temperature of not lower than 1000°C in the lower part of the pre-heater and at the tail of the rotary kiln, and is most suited for carrying out the invention for quickly conducting the disposal without adversely affecting the environment.

25 Further, a desired throwing position in the burning facility for the disposal may be suitably determined depending upon the burning facility. Referring, for example, to the facility for firing the cement, it is most desired to use a calcining furnace
30 in which the gas migrates most vigorously. Further, the tail of the rotary kiln and a position of the rising duct connecting the lower portion of the pre-heater to the tail of the kiln are heated at nearly 1000°C and are suited as throwing positions.

35 Though there is no particular limitation on the

method of throwing the waste developing solution 2 into a predetermined position of the burning facility, it is most desired to throw the waste developing solution in the form of liquid droplets of not larger than 1 mm or by spray for good contact efficiency with the gas in the high-temperature region.

5 (Refining step 7 by dilution)

In the present invention, the waste developing solution 2 containing metal impurities in amounts in excess of the above reference value (50 ppm per the TAA) is not disposed of, but can be fed to the refining step 7 by dilution to use it again.

10 In the refining step 7 by dilution, the developing solution is the TAA hydroxide aqueous solution which has not been used or which contains little impurities, and is used for diluting the waste developing solution 2 to adjust the content of metal impurities in the waste developing solution after diluted to be smaller than the above reference value.

15 The diluted waste developing solution 2 is, then, refined. The refining treatment can be carried out in quite the same manner as the refining treatment shown in Fig. 2. Through the step 7 of dilution, the TAA hydroxide aqueous solution having a high purity can be regenerated for extended periods of time maintaining stability like in the above-mentioned refining step 5.

20 When the contents of metal impurities in the waste developing solution 2 are to be controlled as a total content, the dilution may be so effected that the total content becomes a predetermined reference value (not larger than 200 ppm and, particularly, not larger than 100 ppm per the TAA).

25 As the unused TAA hydroxide aqueous solution to be used for diluting the waste developing solution, there can be favorably used a highly pure TAA

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hydroxide aqueous solution that is used in the step of developing that requires a high precision. The highly pure TAA hydroxide aqueous solution contains impurities in an amount (total amount of various
5 impurities) of not larger than 100 ppb per the TAA, and is prepared as described below.

(Preparation of a highly pure TAA hydroxide aqueous solution)

As shown in Fig. 3, the highly pure hydroxide
10 aqueous solution is produced by using a highly pure starting material A through a reaction step 21 and an electrolyzing step 23.

The highly pure starting material A contains metal ions of each kind in an amount of not larger
15 than 100 ppb, preferably, not larger than 50 ppb and, most preferably, not larger than 10 ppb, or contains impurities in a total amount of not larger than 200 ppb and, particularly, not larger than 100 ppb. Concretely, the tetraalkylammonium salt (TAA salt) is
20 formed by reaction, and there can be used a combination of a trialkylamine and an alkyl chloride, a combination of a trialkylamine, an alkyl formate and a hydrogen peroxide, or a combination of a trialkylamine and a dialkyl carbonate, and any one of
25 them can be used in the form of a highly pure aqueous solution or an aqueous dispersion.

The highly pure starting material A is reacted through the reaction step 21 to form a TAA salt aqueous solution B. This reaction is easily carried
30 out by stirring the highly pure starting material A and, as required, heating the solution at a suitable temperature.

The thus formed TAA aqueous solution B is electrolyzed through the electrolyzing step 23 to
35 obtain a highly pure TAA hydroxide aqueous solution C.

The electrolyzing step 23 is quite the same as the electrolyzing step 13 described above with reference to Fig. 2.

5 The thus obtained highly pure TAA hydroxide
aqueous solution C contains metal ion impurities of
each kind in an amount of not larger than 50 ppb per
the TAA, contains organic impurities stemming from the
unreacted starting materials in a total amount of not
larger than 50 ppm per the TAA, and is useful as a
10 developing solution in the developing step for forming
patterns of a particularly high precision, such as the
developing step for forming fine wiring of a high
density. In the present invention, the thus produced
highly pure TAA hydroxide aqueous solution is used for
15 diluting the waste developing solution 2.
(Regenerated developing solution 17)

 The regenerated developing solution 17 obtained
through the refining step 5 or the refining step 7 by
dilution in accordance with the above-mentioned
20 processing has a very high purity and contains
impurities in amounts of not larger than 10 ppb and
even in a total amount of not larger than 100 ppb, and
contains organic impurities in a total amount of not
larger than 20 ppm.

25 The regenerated developing solution 17 can be
utilized again in the developing step 1 by itself or
being mixed with the unused developing solution, and
can be utilized again as the developing solution even
in the developing step 1 that requires a high
30 precision being mixed with the above-mentioned highly
pure TAA hydroxide aqueous solution.

 When the content of metal impurities in the waste
developing solution 2 exceeds the reference value (50
ppm per the TAA) in the present invention, either the
35 waste disposal step 6 or the refining step 7 by

dilution can be selected. Generally, however, when the total amount of metal impurities contained in the waste developing solution 2 is great, it is desired to select the waste disposal step 6 from the standpoint of decreasing the burden for the diluting and refining treatment which otherwise must be carried out through the refining step 7 by dilution. It is, for example, desired to select the waste disposal step 6 when the total amount of metal impurities is not smaller than 100 ppm and to select the refining step 7 by dilution when the total amount of metal impurities is smaller than 100 ppm.

Further, the treating method of the present invention can be carried out for all of its steps in a factory that carries out the developing step 1 or can be carried out for some of its steps in other place (e.g., in the factory for producing the developing solution). For example, the waste developing solution 2 recovered in the developing step 1 is concentrated and is, then, inspected at the inspection step 4. Depending upon the inspected result, the waste developing solution 2 is transferred to other place and is subjected to the refining treatment through the refining step 5 or through the refining step 7 by dilution. Or, the waste developing solution 2 may be disposed of by burning through the waste disposal step 6. It is allowable to carry out the step after the inspection step 4 in other place, as a matter of course.

When the refining step 5 and the refining step 7 by dilution are installed near the developing step 1, the regenerated developing solution 17 can be circulated and supplied to the developing step 1.

According to the present invention, further, the design can be variously modified. For example, the

concentration step 3 shown in Fig. 1 may be omitted.
Or, the concentration step 3 may be executed after the
inspection step 4 (before, for example, the refining
step 5). Further, the TAA salt solution 15 obtained
5 through the neutralizing/separating step 11 at the
refining step 5 (or at the refining step 7 by
dilution) may be partly supplied to the electrolyzing
step 23 in the process for producing a highly pure TAA
hydroxide aqueous solution.

10 (Examples)

The invention will be described further
concretely by way of Examples to which only, however,
the invention is in no way limited.

Described below are the specifications of the
15 electrolyzer used in the electrolyzing step in the
following Examples.

Electrolyzer:

Filter press electrolyzer having a pair of anode
and cathode of a size of 1 dm² and is sectionalized
20 into an anode chamber and a cathode chamber by a
cation-exchange membrane of a fluorine-contained
resin.

Anode: titanium electrode coated with an oxide

Cathode: nickel electrode

25 Example 1:

A waste developing solution 2 containing a
photoresist and a tetramethylammonium hydroxide (TMAH)
solution discharged from the developing step 1 in a
factory of producing liquid crystal displays (LCDs)
30 was concentrated by using a thin-film concentrator 3
at a solution temperature of 60°C under a reduced
pressure of 20 kPa to obtain a brown concentrated
solution (1).

The concentrated solution (1) that was obtained
35 was analyzed for its components to be as follows:

TMAH concentration: 20.6 wt%

Concentrations of metal impurities:

Al: 3800 ppb (22.7 ppm per TAA)

Na: 40 ppb (0.24 ppm per TAA)

5 Cu: 650 ppb (3.88 ppm per TAA)

Fe: 800 ppb (4.78 ppm per TAA)

Total content per TAA: 31.60 ppm

Total concentration of organic impurities: 3800
ppm

10 The TMAH concentration was measured relying on a
potentiometric titration method, the metal
concentration was measured relying on an ICP-MS
method, and the total concentration of organic
impurities was measured relying on an amount oxygen is
15 consumed by potassium manganate (JIS K 0101).

The above concentrated solution (1) contained
metal impurities in amounts which were smaller than
the reference value (50 ppm) per the TAA, and was,
hence, refined as described below.

20 A CO₂ gas was injected into the concentrated
solution (1) to neutralize it. Near the end of
neutralization, the alkali-soluble resist became
insoluble, and there was formed a precipitate. A
filtering assistant was added in an amount of 1% by
25 weight to the above solution which was, then, passed
through a filter of a pore diameter of 1 µm to
separate the insolubilized precipitate by filtration.

The filtrate (TAA carbonate aqueous solution)
from which the insolubilized matter was separated was
30 concentrated by using a thin-film evaporator at a
solution temperature of 60°C under a reduced pressure
of 20 kPa until the TAA concentration was 30% by
weight.

Next, the concentrated filtrate was electrolyzed
35 by using the above-mentioned electrolyzer. The

conditions of electrolysis were as follows:

Electrolyzing temperature: 50°C

Current density: 20 A/dm²

Total voltage of the electrolyzer: 14 V

5 Treating time: 72 hours

The cathode solution that was obtained after the electrolysis was a colorless transparent solution, and the results of analysis thereof were as follows:

TMAH concentration: 20.9 mass%

10 Concentrations of metal impurities:

Al: 20 ppb or smaller

Na: 20 ppb or smaller

Cu: 20 ppb or smaller

Fe: 20 ppb or smaller

15 Total concentration of organic impurities: 10 ppm or smaller

From the above results of analysis, it was learned that the solution could be used as a developing solution to a sufficient degree.

20 By using the above electrolyzer, the electrolysis was further continued for six months without any trouble.

Comparative Example 1:

25 A waste developing solution 2 containing the photoresist and the TMAH discharged from the developing step 1 in a factory of producing liquid crystal displays (LCDs) was concentrated at a solution temperature of 60°C under a reduced pressure of 20 kPa to obtain a brown concentrated solution (2).

30 The above concentrated solution (2) was analyzed to be as follows:

TMAH concentration: 20.2 wt%

Concentrations of metal impurities:

Al: 12700 ppb (77.3 ppm per TAA)

35 Na: 140 ppb (0.85 ppm per TAA)

Cu: 4800 ppb (29.2 ppm per TAA)
Fe: 3300 ppb (20.1 ppm per TAA)
Total content per TAA: 127.45 ppm
Total concentration of organic impurities: 8100

5 ppm

The above concentrated solution (2) contained metal impurities in amounts which were not smaller than the reference value (50 ppm) of the present invention.

10 The concentrated solution (2) was neutralized, separated and electrolyzed in quite the same manner as in Example 1 to obtain a refined solution. The refined solution was analyzed to be as follows:

TMAH concentration: 20.8 wt%

15 Concentrations of metal impurities:

Al: 45 ppb

Na: 35 ppb

Cu: 40 ppb

Fe: 45 ppb

20 Total concentration of organic impurities: 22 ppm

The refined solution contained impurities in amounts larger than those of Example 1.

The electrolysis was continued by using the electrolyzer. Two months after the start of continuous operation, the membrane potential was elevated due to the wear of the electrodes and deterioration of the cation-exchange membrane, and the operation could no longer be continued.

Example 2:

30 The concentrated solution (2) of Comparative Example 1 was diluted with a highly pure TMAH aqueous solution. The highly pure TMAH aqueous solution and the diluted solution that were used were analyzed to be as follows:

35 Highly pure TMA aqueous solution:

5 TMAH concentration: 20.1 wt%
Al: 5 ppb or smaller
Na: 5 ppb or smaller
Cu: 5 ppb or smaller
Fe: 5 ppb or smaller
Total concentration of organic impurities:
10 ppm or smaller

Diluted solution
10 TMAH concentration: 20.3 wt%
Al: 6000 ppb (36.3 ppm per TAA)
Na: 60 ppb (0.36 ppm per TAA)
Cu: 2100 ppb (12.7 ppm per TAA)
Fe: 1500 ppb (9.01 ppm per TAA)
Total content per TAA: 58.37 ppm
15 Total concentration of organic impurities:
3800 ppm

The above diluted solution contained metal
impurities in amounts which were smaller than the
reference value (50 ppm) of the present invention.
20 By using the diluted solution, a refined solution
was obtained by conducting the neutralization,
separation and electrolysis in quite the same manner
as in Example 1. The refined solution was analyzed to
be as follows:

25 TMAH concentration: 20.5 wt%
Concentrations of metal impurities:
Al: 20 ppb or smaller
Na: 20 ppb or smaller
Cu: 20 ppb or smaller
30 Fe: 20 ppb or smaller
Total concentration of organic impurities: 10 ppm
or smaller

From the above results of analysis, it was
learned that the refined solution could be used as a
35 developing solution to a sufficient degree.

By using the above electrolyzer, the electrolysis was further continued for six months without any trouble.

Example 3:

5 The concentrated solution (2) (waste developing solution) of Comparative Example 1 was supplied as liquid droplets or mist to the portions (temperatures are shown as well) in a process for producing a cement shown in Table 1. The waste developing solution was
10 continuously thrown in an amount to be about 10 g/Nm³ relative to the gas flow rate at the thrown portion.

Table 1 shows a drop of temperature of the flue gas exhausting the gas from the pre-heater after the TAA-containing waste developing solution was thrown.
15 Table 1 further shows the results of detecting amines such as trimethylamine in the flue gas exhausting the gas from the pre-heater.

20

Table 1

No.	Position of throwing waste <u>solution</u>		Supplying <u>method</u>	Drop of temp. of flue <u>gas</u>	Presence of amines in the <u>flue gas</u>	
	<u>Place</u>	<u>Temp.</u>				
25	1	calcining Furnace	950°C	droplets	no	no
30	2	kiln	1000°C	mist	no	no

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Claims:

1. A method of treating a waste developing solution recovered from a photoresist-developing step where a tetraalkylammonium hydroxide aqueous solution is used as a developing solution, comprising:

measuring a concentration of tetraalkylammonium and contents of metal impurities in the waste developing solution;

when the contents of the metal impurities are all not more than 50 ppm per the tetraalkylammonium, refining the waste developing solution to regenerate the tetraalkylammonium hydroxide solution so as to be used as the developing solution; and

when the content of at least one kind of metal impurity is more than 50 ppm per the tetraalkylammonium, diluting the waste developing solution with a highly pure tetraalkylammonium hydroxide aqueous solution so that the content of the metal impurity that was greater than 50 ppm becomes smaller than 50 ppm, and refining the waste developing solution that is diluted to regenerate the tetraalkylammonium hydroxide aqueous solution so as to be used as the developing solution.

2. A method of treating waste developing solution according to claim 1, wherein the treatment for refining the waste developing solution or the diluted waste developing solution includes a neutralizing/separating step of precipitating the photoresist by neutralizing the tetraalkylammonium hydroxide in the waste developing solution or in the diluted waste developing solution and separating the precipitated photoresist, and an

electrolyzing step of forming the tetraalkylammonium hydroxide by electrolyzing a solution that contains a tetraalkylammonium salt obtained through the neutralizing/separating step.

3. A treating method according to claim 1, wherein a highly pure tetraalkylammonium hydroxide aqueous solution containing impurities in a total amount of not larger than 100 ppb per tetraalkylammonium is used as a solution for diluting the waste developing solution.

4. A method of treating waste developing solution according to claim 2, wherein the waste developing solution is so concentrated that the concentration of the tetraalkylammonium hydroxide in the waste developing solution becomes not lower than 8 mass%, and the concentrated waste developing solution is supplied to the neutralizing/separating step.

5. A method of treating a waste developing solution according to claim 1, wherein the waste developing solution is refined to regenerate the tetraalkylammonium hydroxide solution so as to be used as the developing solution when the contents of the metal impurities are all not more than 50 ppm per the tetraalkylammonium and when the total content of the metal impurities is not more than 120 ppm, wherein when the total content of the metal impurities is more than 120 ppm, the waste developing solution is diluted with a highly pure tetraalkylammonium hydroxide aqueous solution so that the total content of the metal impurities becomes not more than 120 ppm, and the diluted solution is refined to regenerate the tetraalkylammonium hydroxide aqueous solution so as to be used as the developing

solution.

6. A method of treating a waste developing solution according to claim 1, wherein the regenerated tetraalkylammonium hydroxide aqueous solution is used again being mixed with the unused tetraalkylammonium hydroxide aqueous solution which is the developing solution.

7. A treating method according to claim 6, wherein a highly pure tetraalkyl ammonium hydroxide aqueous solution containing impurities in a total amount of not larger than 100 ppb per tetraalkyl ammonium is used as the unused tetraalkylammonium hydroxide aqueous solution.