

DESCRIPTION

Method for Reusing Waste Etching Liquid

5 TECHNICAL FIELD

The present invention relates to a method for reusing a waste liquid generated during an etching process, in which a copper article is etched while using an ammonical alkaline cupric chloride etchant, by
10 continuously and selectively extracting copper from the waste liquid by using an extraction solvent.

BACKGROUND ART

As the etching liquids which are used in the production process for printed circuit boards, an
15 alkaline type or an acid type is selectively used in accordance with the kinds of resists adopted in the process. Recently, due to the severe economic circumstances, the acid type etching liquid has been increasingly used due to its lower running cost.

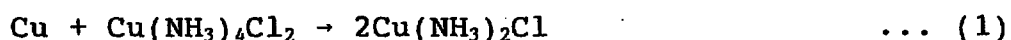
20 It is difficult, however, to completely replace the alkaline type by the acid type, because highly integrated circuit boards have recently been advantageously produced through a pattern plating method, and there are kinds of printed circuit boards which are impossible to produce
25 unless a metallic resist is used.

An object of the present invention is to carry out the etching operation while using the alkaline type etching liquid at a lower running cost compared with the acid type etching liquid, by reusing the alkaline etching
30 liquid which is refreshed by the extraction solvent.

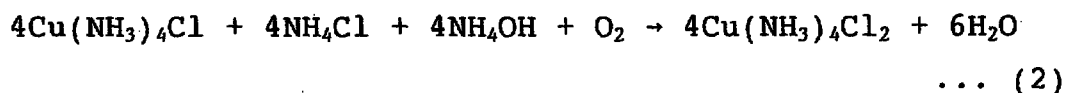
The ammoniac alkaline etching liquid used in the process for producing the printed circuit boards is mainly used for erosively removing useless copper other than necessary copper circuit patterns covered with an
35 anti-erosive metal against ammoniac alkali as an etching resist, such as a solder plating layer or a nickel plating layer.

The etching liquid consists of an operating-bath liquid mainly comprised of cupric chloride forming ammoniac complex, aqueous ammonia and ammonium chloride; a replenishing liquid mainly comprised of ammonium chloride and aqueous ammonia; and various additives for, for example, preventing the solder from erosion, improving the complexing ability, enhancing the etching accuracy, and accelerating and stabilizing the etching rate.

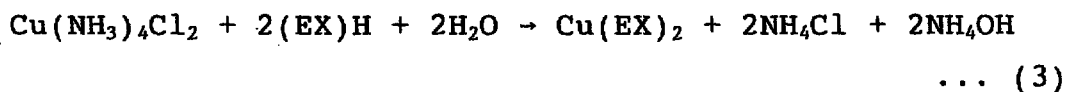
The etching operation is carried out by using the oxidizing ability of bivalent copper as represented by the following formula (1):



According to an ordinary regeneration system wherein the conventional replenishing liquid is used, copper (I) formed by the reduction during the etching process as represented by formula (1) is restored to original copper (II) as represented by the following formula (2), and then the etching liquid is diluted to have a lower copper content for the purpose of reuse.



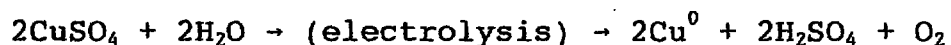
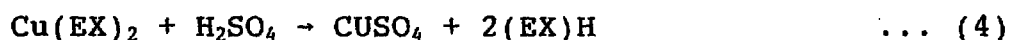
A method for collecting metal by extraction while using an organic solvent insoluble in water has been very popular in the mining industry. Copper in the etching liquid is collected in a way represented by the following formula (3);



wherein copper is favorably collected by sufficiently mixing the waste etching liquid with an extraction solvent.

As for the collection of copper from the extraction solvent, copper sulfate is obtained by sufficiently mixing the extraction solvent with the aqueous solution of sulfuric acid as represented by formula (4), from

which copper can easily be collected by electrolysis as represented by formula (5).



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The United States Patent No. 4,083,758 or Japanese Unexamined Patent Publication (Kokai) No. 62-53592 discloses a method for regenerating a waste alkaline etching liquid by using an extraction solvent.

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The former is characterized by the provision of a rinsing process for removing chloride ions extracted simultaneously with the extraction of copper ions, and the latter is characterized by the provision of an extraction process for collecting copper contained in rinsing water used after the etching.

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However, the rinsing process for removing chloride ions provided in the former has recently been unnecessary because it is possible, by the selection of a proper extraction solvent, to reduce an intake amount of chloride ions to such an extent as to have a negligible influence upon the collection of copper by electrolysis after back extraction.

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While the latter process is advantageous in the collection of copper in the rinsing water, it has a drawback in that a large amount of copper hydroxide may be generated when the rinsing water passes through the same cycle, which is a cause of the disturbance of a total balance in the system.

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More concretely, there may be a choking of a piping system, including an extraction device for rinsing water, or a breakage of a rinsing pump for an etching liquid.

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Addition of a considerable amount of aqueous ammonia is one solution for such problems. However, it is difficult to maintain a proper concentration of ammonia because a total amount of rinsing water is large. In addition, an ammonia odor becomes intense around the

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etching process to deteriorate the working environment as well as to exert a bad influence upon the operator's health.

DISCLOSURE OF THE INVENTION

5 An object of the present invention is to solve the above-mentioned problems of the prior art and to provide a method for reusing a waste etching liquid capable of smoothly carrying out an etching operation through a safe and stable solvent extraction cycle.

10 That is, the waste etching liquid of an alkaline type is regenerated by extraction so that it can be reused for a longer period in the etching process while maintaining a good performance.

15 A small number of sulfate groups, derived from a saponificated layer or the like formed by the repetition of contact of the extraction solvent with the alkaline etching liquid for a long period, are contained in the solvent separated through the back extraction and will easily migrate into the alkaline etching liquid after
20 reuse of the extraction solvent as it is. There may be problems if the sulfate groups enter the etching liquid in that, immediately, an etching rate becomes unstable, and, in the long run, crystals may separate out in the etching liquid if the temperature is lowered. Further,
25 since the sulfate group has a large specific weight, the apparent specific weight of the etching liquid increases thereby. Accordingly, in an ordinary alkaline type etching system in which the replenishment of fresh liquid is indicated in accordance with the variation of specific
30 weight, the concentration of copper is liable to decrease, which in turn results in the lowering of etching rate or the deterioration of etching accuracy.

35 To eliminate such drawbacks, according to the present invention, the sulfate groups mixed into the etching liquid during the back extraction are removed by rinsing the extraction solvent after the back extraction. And the extracted liquid is reused for the extraction of

the alkaline etching liquid so that the long term use of the alkaline etching liquid is possible in a stable manner.

That is, according to the present invention, a method is provided for reusing a waste liquid generated during an etching process wherein a copper article is etched while using an ammoniac alkaline cupric chloride etchant, by continuously and selectively extracting copper from the waste liquid by using an extraction solvent, characterized in that the method comprises:

(a) a process for continuously agitating and mixing the waste liquid and the extraction solvent and separating the mixture into an extraction solvent containing copper and a regenerated liquid having a reduced copper concentration, while reusing the regenerated liquid having the reduced copper concentration for the etching operation;

(b) a back extraction process for agitating and mixing the extraction solvent containing copper extracted from the waste liquid and an aqueous solution of sulfuric acid and copper sulfate prepared so that the concentrations of copper and sulfuric acid are maintained in a predetermined range, and separating the mixture so that copper in the extraction solvent migrates into the aqueous solution of sulfuric acid and copper sulfate;

(c) a process for rinsing the extraction solvent which has been separated through the back extraction process, by using a rinsing liquid such as cold water, hot water or dilute hydrochloric acid, to remove sulfuric acid therefrom;

(d) a process for reusing the extraction solvent thus rinsed for the extraction and regeneration of the waste etching liquid; and

(e) a process for collecting metallic copper from the aqueous solution of sulfuric acid and copper sulfate having an increased copper concentration due to the back extraction through the electrolysis thereof.

Accordingly, one of the most important features of the present invention resides in that the extraction solvent separated through the back extraction is rinsed by cold water, hot water or, preferably, dilute hydrochloric acid. In this connection, some types of extraction solvent may have problems in the separation from the aqueous system caused by the affinity to the aqueous system or the difference in the specific weight therebetween. In such cases, an aqueous solution of a composition contained in the etching liquid, which has no adverse effect even though mixed with the etching liquid, can be used as the rinsing liquid.

According to one aspect of the present invention, it is characterized in that the etching liquid regenerated by the extraction solvent passes through an oil absorbent member or an oil/water separation membrane for removing an amount of extraction solvent taken therein. Since the taken-in extraction solvent is removed when the etching liquid regenerated by the extraction solvent passes through the oil absorbent member or the oil/water separation membrane, it will be possible to properly reuse the regenerated etching liquid.

According to another aspect of the present invention, it is characterized in that after the aqueous solution of sulfuric acid and copper sulfate separated through the back extraction has passed through the oil absorbent member or the oil/water separation membrane for the purpose of removing an amount of the extraction solvent taken in the aqueous solution, copper contained therein is collected as metallic copper in an electrolysis bath. Also, the aqueous solution of sulfuric acid and copper sulfate separated through the back extraction is circulated to the electrolysis bath via an intermediate bath provided with an oil absorbent member for removing an amount of the extraction solvent taken in the generated liquid and copper contained therein is collected as metallic copper in an

electrolysis bath. In such cases, since an amount of the taken-in extraction solvent is removed from the aqueous solution of sulfuric acid and copper sulfate separated through the back extraction during the passage through the oil absorbent member or the oil/water separation membrane, the collection of metallic copper can be smoothly carried out by electrolysis.

According to still other aspects, it is characterized in that, in the process for separating the mixture of waste etching liquid and extraction medium into the original components after the both have been continuously agitated and mixed, the mixture passes through a plurality of partitions with apertures, having diameters which become smaller closer to an exit of a separation bath, for the purpose of reliably carrying out the separation within a short period. By passing the mixture through the plurality of partitions with the above mentioned apertures, it is possible to carry out the separation within a shorter period due to the collision of small particles of the extraction solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an overall construction of a system according to the present invention based on a liquid circulation path;

Fig. 2 illustrates a mixer-settler (MS-1) used in an extraction process;

Fig. 3 illustrates mixer-settlers (MS-2 and MS-3) used in a back extraction process and a rinsing process, respectively;

Figs. 4 and 5 illustrate a device according to one embodiment of the present invention;

Fig. 6 illustrates a circulation path of a comparative example;

Fig. 7 is a graph for illustrating the change of a concentration of sulfuric acid in the etching liquid relative to the operating months; and

Fig. 8 is a graph for illustrating the change of an

etching rate relative to the months of operation.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in more detail below with reference to the preferred embodiments
5 illustrated in the attached drawings.

Fig. 1 illustrates an overall construction of a system according to the present invention based on a liquid circulation path. The respective materials continuously flow under control.

10 Initially, a waste liquid discharged from an etching process and an extraction solvent capable of effectively and selectively extracting copper are fed to a mixer-settler MS-1 while maintaining a predetermined flow ratio therebetween, and agitated and mixed together in a
15 mixer section to form a mixture solution. While the mixture solution is transported at a low speed in a settler section, it is separated into a regenerated etching liquid having a reduced copper concentration and an extraction solution containing copper. A favorable
20 extraction solvent capable of selectively extracting copper is a solvent reagent, for example, of a β -di-ketone type or an oxime type added with a diluting solution consisting of kerosine having a boiling point of about 200°C.

25 Fig. 2 shows the mixer-settler MS-1 used therein. The mixture solution prepared in the mixer section M passes through a filter 31 to flow into the settler section S constituting a separation bath. A plurality of partitions 32 with apertures, having diameters which
30 become smaller closer to an exit, are arranged in the settler section S at a predetermined gap between every adjacent partitions. It has been confirmed from a test that dispersed particles of extraction solvent tend to collide to each other when passing through the
35 partitions 32, and are separated from the mixture solution within a shorter period. In the settler section S are formed a lower layer of a regenerated etching

liquid having a reduced copper concentration and an upper layer of an extraction solvent containing copper, which layers are collected, respectively, on the exit side.

5 The regenerated etching liquid from which copper has been extracted passes through an oil absorbent member to remove a very small amount of extraction solution left therein and is returned to the etching process to be reused therefor.

10 The extracted solvent containing copper is transferred to MS-2. An aqueous solution of sulfuric acid (aqueous solution of sulfuric acid and copper sulfate) of a predetermined ratio relative to a transferred amount of the extraction solvent containing copper is supplied to a mixer-settler MS-2. Both
15 components are mixed in a mixer section and separated from each other during the transportation at a lower speed in a settler section contiguous to the mixer section.

20 Copper dissolved in sulfuric acid as copper sulfate passes through the oil absorbent member as an aqueous solution of sulfuric acid and copper sulfate to remove a taken-in amount of the extraction solvent, then is transferred to an electrolysis bath and collected as a valuable substance in the shape of metallic copper
25 through the electrolysis. The diluted sulfuric acid after the collection of metallic copper (wherein copper is still left as copper sulfate at 10% to 15% concentration) is reused in the mixer-settler MS-2.

30 While both of the regenerated etching liquid and the aqueous solution of sulfuric acid and copper sulfate used for the back extraction are transferred to the etching process and the electrolysis process after passing through the oil absorbent member, there may be a problem of the reduction of the etching rate if a large amount of
35 extraction solvent is mixed with the etching liquid, and of a disturbance of electrolysis due to the inferior conductivity of electrodes if the extracted solvent is

mixed in an electro-deposition tank for the electrolysis.

Of course, it is possible to preliminarily remove the extraction solvent from such a mixture by using active carbon. However, active carbon is very expensive and the absorbability thereof is too low to achieve the object of the present invention. Also, the absorption rate thereof is lower than that of the oil absorbent member. The oil/water separation membrane may be used for this purpose. Needless to say, it may be possible to preliminarily remove the mixed extraction solvent by the oil absorbent member and then filtrate the regenerated etching liquid through the active carbon so that the load on the active carbon is mitigated.

According to the confirmation test, a favorable removal of the extraction solvent was obtainable solely by the use of an oil absorbent member "Oilock 100" (phonetic) available from Kawasaki Sanko Kasei K.K.

The extraction solvent from which copper has been removed is transferred to a mixer-settler MS-3.

A process for rinsing the extraction solvent according to MS-3 is very important for operating this system in a stable manner for a long period, wherein the extraction solvent is rinsed with cold water, hot water or preferably an aqueous solution containing a diluted hydrochloric acid or a predetermined amount of a component contained in the etchant. It is possible by this process to completely rinse sulfate groups taken in the solvent whereby the extraction solvent is restored to the original state.

This rinsing process may be carried out by spraying water to the extraction solvent flowing along a flat surface or a surface of a three-dimensional structure, which minimizes the space necessary for the installation.

Fig. 3 illustrates a combination of a mixer-settler MS-2 for carrying out the back extraction and a rinsing device MS-3 of such a spray type. In the mixer-settler MS-2, as described before, the extraction solvent and the

diluted sulfuric acid (aqueous solution of sulfuric acid and copper sulfate) are agitated and mixed together in a mixer section M to form a mixture which flows through a filter 41 into a settler section S used as a separation tank in a similar manner as in the mixer-settler MS-1. The settler section S has a plurality of partitions 42, arranged at a predetermined pitch, with apertures having diameters which become smaller closer to an exit in the same manner as described with reference to MS-1, for the purpose of facilitating the separation. In the settler section S, a lower layer of the aqueous solution of sulfuric acid and copper sulfate and an upper layer of the extraction solvent are formed due to the separation, and the extraction solvent overflowing the exit 43 runs down along a slanted surface 44 constituting a mixer section of MS-3 while being mixed with a rinsing water sprayed from above.

A settler section of MS-3 also has a plurality of partitions 46 with apertures having diameters which become smaller closer to an exit in the same manner as described before. The rinsing water in the lower layer is pumped up by a pump 47 and reused as a rinsing water, and the extraction solvent in the upper layer restored to the original state is collected and reused for the extraction of copper in the mixer-settler MS-1.

Figs. 4 and 5 illustrate an embodiment of an apparatus for carrying out the method for reusing the waste etching liquid according to the present invention. The regenerated etching liquid in a regenerated etching liquid tank 1 is stored in a regenerated liquid intermediate tank 14 and supplied to an etching bath E. After the etching operation, a waste liquid is stored in a waste etching liquid storage tank 3 via a waste etching liquid intermediate tank 15 (a part of the liquid is stored in the storage tank 3 via an operating-bath liquid reserve tank 16).

The waste etching liquid is stored in a waste liquid

intermediate tank 5 and then mixed and separated in an etchant extraction/regeneration tank 6 (MS-1) as described before. A regenerated etching liquid thus separated is stored in a regenerated etchant collecting
5 tank 7 and then returned to the regenerated etching storage tank 7.

An extraction solvent is stored in a collecting tank 8 and then mixed and separated in a back extraction tank 9 (MS-2) as described before. The back-extracted
10 solvent is collected in a collecting tank 10 and rinsed in an extraction solvent rinsing tank 11. Collected rinsing water is reused via a circulating tank 12. The extraction solvent thus rinsed is reused in the etchant extraction/regeneration tank 6 (MS-1).

15 An aqueous solution of sulfuric acid and copper sulfate separated in the back extraction bath 9 (MS-2) is transported via an oil absorbent member 19 to electro-deposition tanks 20, 21 in which it is subjected to an electrolysis operation while a voltage is rectified by
20 rectifiers 24 and 25. Thus, metallic copper is collected. The aqueous solution returned from the electro-deposition tanks 20, 21 is reused in the back extraction tank 9 (MS-2) via a relay tank 18 for the electro-deposition tanks.

25 In an aqueous ammonia storage tank 2 is stored a fresh etching liquid containing aqueous ammonia which is added, if required, to the etching tank E via an aqueous ammonia intermediate tank 17, or to the regenerated etching liquid storage tank 1 via a fresh liquid
30 preparation tank 4.

These liquid flows are all controlled by pumps P in a continuous and automatic manner.

Tests for confirming the effect of the present invention were carried out while using the actually
35 operating extraction/regeneration apparatus shown in Figs. 4 and 5. Results thereof are described in Table 1 below:

Table 1

Continuous Operating Period for Etching with or without Rinse after Extraction

Conditions	Maximum period for etching liquid to be renewed
Without rinse	3 months
With rinse only after extraction (Comparative Example)	3 months
With rinse only after back extraction (Example)	There was no trouble at all even after one year.

In these confirmation tests, "without rinse" means that the extraction solvent back-extracted in MS-2 is reused in MS-1 without being rinsed in MS-3, as shown by dotted lines in Fig. 1. "With rinse only after extraction" means that the extraction solvent is rinsed after being extracted in MS-1 and then back-extracted, as shown in Fig. 6 as a comparative example.

When the rinsing process is eliminated or carried out only after the extraction of copper from the etching liquid, the etching rate is lowered and the etching accuracy becomes worse within a shorter period of three months, which necessitates the replacement of a whole amount of expensive etching liquid with a fresh one.

According to the investigation into which compositions deteriorate in the etching liquid, it was found, as shown in Fig. 7, that sulfuric acid used in the back extraction process migrates into the etching liquid via the extraction solvent.

That is, as is apparent from Fig. 7, when the rinsing process is not used, the sulfuric acid concentration rises as the time of operation increases, which indicates that the sulfuric acid used in the back-extraction process is taken into the etching liquid.

Also, as sulfate groups are taken into the regenerated etching liquid, the etching rate is lowered

as the time of operation increases as shown in Fig. 8.

On the contrary, according to the embodiment of the present invention in which the rinsing process is incorporated in the system after the back extraction process, the sulfuric acid concentration does not rise as shown in Fig. 7 and the etching rate is not lowered as shown in Fig. 8, because the sulfate groups are not mixed into the etching liquid. Therefore, it is possible to continuously carry out the etching operation in a stable manner and repeat the regeneration of the etching liquid by the extraction of solvent.

In such confirmation tests, a fresh etching liquid was properly replenished to compensate for a taken-out amount of etching liquid.

While the present invention was described in detail above with reference to the preferred embodiments illustrated in the attached drawings, it is noted that the present invention should not be limited to the above embodiments but includes various modifications and changes without departing from a spirit or scope of the present invention.

CAPABILITY OF EXPLOITATION IN INDUSTRY

As described above, according to the present invention, since the sulfate groups mixed into the extraction solvent during the back extraction process are removed by rinsing the same after the back extraction, no sulfate groups are taken into the etching liquid. Therefore, it is possible to use the etching liquid for a long period in a stable manner.

CLAIMS

1. A method for reusing a waste liquid generated during an etching process wherein a copper article is etched while using an ammoniac alkaline cupric chloride etchant, by continuously and selectively extracting copper from the waste liquid by using an extraction solvent, characterized in that the method comprises:

(a) a process for continuously agitating and mixing the waste liquid and the extraction solvent and separating the mixture into an extraction solvent containing copper and a regenerated liquid having a reduced copper concentration, while reusing the regenerated liquid having the lower copper concentration for the etching operation;

(b) a back extraction process for agitating and mixing the extraction solvent containing copper extracted from the waste liquid and an aqueous solution of sulfuric acid and copper sulfate prepared so that the concentrations of copper and sulfuric acid are maintained in a predetermined range, and separating the mixture so that copper in the extraction solvent migrates into the aqueous solution of sulfuric acid and copper sulfate;

(c) a process for rinsing the extraction solvent which has been separated through the back extraction process, by using a rinsing liquid such as cold water, hot water or dilute hydrochloric acid to remove sulfuric acid therefrom;

(d) a process for reusing the extraction solvent thus rinsed for the extraction and regeneration of the waste etching liquid; and

(e) a process for collecting metallic copper from the aqueous solution of sulfuric acid and copper sulfate, having an increased copper concentration due to back extraction, through the electrolysis thereof.

2. A method for reusing a waste liquid as defined by claim 1, characterized in that the etching liquid regenerated by the extraction solvent passes through an



oil absorbent member or an oil/water separation membrane for removing an amount of extraction solvent taken therein.

5 3. A method for reusing a waste liquid as defined
by claim 1, characterized in that after the aqueous
solution of sulfuric acid and copper sulfate separated
through the back extraction has passed through the oil
absorbent member or the oil/water separation membrane for
the purpose of removing an amount of the extraction
10 solvent taken in the regenerated liquid, copper contained
therein is collected as metallic copper in an
electrolysis bath.

 4. A method for reusing a waste etching liquid as
defined by claim 3, characterized in that the aqueous
15 solution of sulfuric acid and copper sulfate separated
through the back extraction is circulated to the
electrolysis bath via an intermediate bath provided with
an oil absorbent member for removing an amount of the
extraction solvent taken in the aqueous solution, and
20 copper contained therein is collected as metallic copper
in the electrolysis bath.

 5. A method for reusing a waste etching liquid as
defined by claim 1, characterized in that, in the process
for separating the mixture of waste etching liquid and
25 extraction medium into the original components after the
both have been continuously agitated and mixed, the
mixture passes through a plurality of partitions with
apertures, having diameters which become smaller closer
to an exit of a separation bath, for the purpose of
30 reliably carrying out the separation within a short
period.

