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1 PROCESS AND APPARATUS FOR TREATING COPPER CHLORIDE ETCHING
WASTE LIQUOR

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BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to a process and an apparatus for treating the copper chloride etching waste liquor which has been discharged from copper chloride etching apparatuses employed, for example, in the process of producing printed wiring boards.

(b) Description of the Related Art

15 In the production of printed wiring boards, circuits are generally made by using an etching method, wherein the copper foil on copper-clad laminates or the copper layer of electroless copper plated boards is etched with an etchant of aqueous iron chloride or copper chloride
20 solution to dissolve the parts unnecessary for the circuits. During the etching, in order to prevent the deterioration of etching capacity due to the dissolution of copper, the etchant is regenerated and is adjusted to a uniform concentration by addition of desired agents, which
25 generates increment liquid to be discharged from etching



1 apparatuses as an etching waste liquor. The etching waste
liquor is collected generally by the etchant makers or the
industrial waste disposal or treatment trade, where it is
regenerated or treated by various methods.

5 However, the recent increase of the waste liquor
becomes a serious problem since it is worsening the
transporting circumstances and is making the regeneration
capacity reach to limit, thereby causing a surge in the
regeneration and treatment costs. It, therefore, is no
10 longer possible to depute the treatment and regeneration to
the outside makers or the like, and there is an increasing
demand for the techniques that enables the most desirable
solution, namely the techniques for completing the
treatment or regeneration at the sources of the etching
15 waste liquor at a low cost. Known techniques for treating
or regenerating the etching waste liquor include
substitution of iron chloride etching waste liquor and
electrolytic treatment of copper chloride etching waste
liquor, which is disclosed in Japanese Patent Application
20 Kokai Koho (Laid-open) No. 02-254188.

 The substitution of iron chloride etching waste
liquor, which is a mixed solution of iron chloride and
copper chloride, is a method based on the tendency of iron
and copper to ionization, wherein steel is added into an
25 etching waste liquor to deposit copper on the steel,



1 thereby forming a fresh iron chloride etchant. The method,
however, provides iron chloride etchant in a large amount
exceeding demand, and resulting iron-copper composition,
which is in itself an important metal resource, is used
5 like a by-product close to waste because of the difficulty
in separating each ingredient.

By the electrolytic treatment of copper chloride
etching waste liquor disclosed in the Japanese Patent
Application Kokai Koho (laid-open) No. 02-254188, copper is
10 deposited on the cathode and is recovered as metal copper.
The process, however, requires an environmental measure to
counter the gaseous chlorine which generates simultaneously
at the anode. Further, the peeling and collection of the
electrodeposited copper from the cathode requires many
15 hands, and the automation of these procedures needs
expensive equipment. There is another problem in that even
the electrodeposited copper of high purity contains trace
ingredients of the etching waste liquor, so that the reuse
thereof also requires costly purification. Furthermore,
20 although the electrolytic treatment is advantageous in that
the regenerated liquid resulting from the removal of copper
is reusable as an etchant, the electrolysis consumes much
electricity, and this method may be difficult to smoothly
link to the control and regeneration of etchant used in
25 actual etching apparatuses.

1 As a method of treating iron-steel acid wash
waste liquor, a process for obtain powdery iron oxides and
aqueous hydrochloric acid solution by roasting an aqueous
iron chloride waste is disclosed in Iron and Steel, No. 70,
5 Vol. 14, 1984, Tasuo Obi, Takehiko Ohkubo, "Novel method of
treating iron-steel acid wash waste by fluidized roasting"
and Japanese Patent Application Kokai Koho (Laid-open) No.
63-315519.

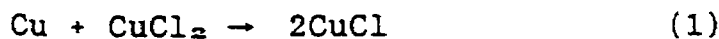
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SUMMARY OF THE INVENTION

The object of the present invention is to provide
a process and an apparatus for efficiently treating copper
15 chloride etching waste liquor, and recovering industrially
useful materials.

Copper chloride etchant is an aqueous solution
containing cupric chloride as a main component. The method
of etching copper with copper chloride etchant is a
20 chemical method wherein copper is dissolved and removed
following the reaction formula (1).

Etching



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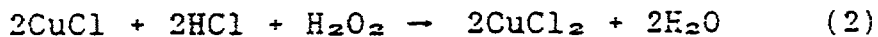
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1 The cuprous chloride resulting from the
dissolution of copper slows down the rate of etching.
Therefore, hydrochloric acid and hydrogen peroxide are
added to the etchant to regenerate and control the cuprous
5 chloride to a low concentration. The regeneration is
expressed by the following reaction formula (2).

Regeneration



10

That is, etching of one mol of copper causes one
mol excess cupric chloride and two moles excess water, and
the increment liquor due to the excess products is
discharged from etching apparatuses. Since etching
15 apparatuses are operated with the etchant kept to a
constant concentration, the increment liquor is generally
allowed to overflow the etchant circulating tanks installed
under the etching apparatuses.

Herein, "copper chloride etching waste liquor"
20 means the waste liquor discharged from the above-mentioned
copper chloride etching for etching copper, and is an
aqueous solution containing cupric chloride, hydrochloric
acid, cuprous chloride and small amounts of other
impurities. The copper chloride etching waste liquor
25 generally contains 20 to 30 % by weight of cupric chloride.



1 3 to 5 % by weight of hydrochloric acid and 0.1 to 0.3 % by
weight of cuprous chloride. That is, the waste liquor is a
rich resource of copper and chlorine, which may be
regenerated into various copper materials and into
5 hydrochloric acid for the above-mentioned regeneration
uses, respectively.

The inventors made study on the methods for
treating the copper chloride etching waste liquor and found
that that cupric oxide and hydrochloric acid are obtainable
10 by exposing the copper chloride etching waste liquor to a
high-temperature atmosphere by, for example, roasting. On
the basis of the finding, they completed the present
invention.

That is, the present invention is based on the
15 inventors' novel conception of using thermal decomposition
reactions for treating copper chloride etching waste liquor
and also on the results of their experiments, from which it
was confirmed that cupric oxide and hydrochloric acid could
actually be obtained and be reused industrially.

20 The present invention provides a process for
treating copper chloride etching waste liquor which
generates in a process for etching copper with a copper
chloride etchant, comprising: exposing said copper chloride
etching waste liquor to an atmosphere of a high temperature
25 ranging from 450 to 1,200 °C in the presence of oxygen to



- 1 generate cupric oxide and hydrogen chloride, separating
said cupric oxide and said hydrogen chloride, collecting
the separated cupric oxide, dissolving the separated
hydrogen chloride into water to form hydrochloric acid, and
5 collecting said hydrochloric acid.

The present invention also provides an apparatus
for treating copper chloride etching waste liquor which
generates in a process for etching copper with a copper
chloride etchant, comprising:

- 10 (a) a roasting furnace for exposing said copper
chloride etching waste liquor, which has been concentrated
in a concentrating tower, to an atmosphere of a high
temperature ranging from 450 to 1,200 °C, in the presence
of oxygen, to generate cupric oxide and a gas mixture
15 containing hydrogen chloride and vapor,

(b) a cyclone for separating and collecting said
cupric oxide from said gas mixture,

- (c) a cooling tower for cooling remaining cupric
oxide and said gas mixture which have been discharged from
20 the cyclone to a temperature of 400 to 500 °C,

(d) an electrostatic precipitator for
electrically separating and collecting said remaining
cupric oxide from said gas mixture,

- (e) a concentrating tower for concentrating
25 said copper chloride etching waste liquor by bringing said



1 copper chloride etching waste liquor into contact with said
gas mixture which has been discharged from said
electrostatic precipitator,

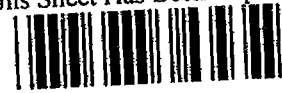
(f) a hydrochloric acid collecting tower for
5 bringing water into contact with said gas mixture which has
been discharged from the concentrating tower after the
contact with said copper chloride etching waste liquor, to
dissolve said hydrogen chloride contained in said gas
mixture into said water and to collect resulting
10 hydrochloric acid, and

(g) a gas cleaning tower for cleaning an exhaust
gas which has been discharged from said hydrochloric acid
collecting tower and contains remaining hydrogen chloride,
by neutralizing said exhaust gas with an aqueous alkali
15 solution.

BRIEF DESCRIPTION OF THE DRAWING

20 Fig. 1 is a flow diagram illustrating an
embodiment of the process of the present invention and the
uses of the cupric oxide and hydrochloric acid which are
collected by the process of the present invention.

Fig. 2 is a graph showing the relationship
25 between the temperatures in a roasting furnace and the



1 percentages of cupric chloride dihydrate and cupric oxide
in the resulting copper compounds.

Fig. 3 is a flow diagram illustrating an
embodiment of the process of the present invention and an
5 embodiment of the apparatus of the present invention.

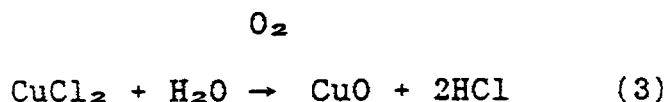
DESCRIPTION OF THE PREFERRED EMBODIMENT

10 Fig. 1 shows an embodiment of the process of the
present invention applied to the treatment of a copper
chloride etching waste liquor which has been discharged
from a copper chloride etching apparatus used in the
developing-etching-peeling stage of a circuit-making
15 process in the production of printed wiring boards, wherein
the copper chloride etching waste liquor is thermally
decomposed according to the process of the present
invention to collect cupric oxide and hydrochloric acid.
The collected cupric oxide can be reused for regenerating
20 copper chloride etchant. On the other hand, the collected
cupric oxide can be dissolved into aqueous sulfuric acid
solution by using a dissolution reactor to use as a
material for the production of copper foil in a process of
producing printed wiring boards or as a replenishing copper
25 source for the copper sulfate bath for chemical copper



1 plating or copper electroplating. The cupric oxide can
also be used as a copper material, for example, for the
production of copper paste or superconductor or powder
metallurgy by, for example, mixing it with other materials,
5 followed by various processings and forming.

According to the present invention, a copper
chloride etching waste liquor is first exposed to a high-
temperature atmosphere, to generate cupric oxide and
hydrogen chloride. The generation of cupric oxide and
10 hydrogen chloride is presumed to be expressed by the
following reaction formula (3).



15

Fig. 2 shows the relationship between the
temperatures in a roasting furnace, where a copper chloride
etching waste liquor is exposed to a combustion gas of
kerosine, and the percentages of cupric chloride dihydrate
20 and cupric oxide in the product copper compounds. From the
results of the inventors' experiments, as shown in Fig. 2,
the generation of cupric oxide begins at about 400 °C , and
almost all cupric chloride is oxidation-decomposed into
cupric oxide at a temperature in the roasting furnace of
25 about 550 °C . According to the present invention,



1 therefore, a copper chloride etching waste liquor is
brought into contact with a high-temperature atmosphere at
a temperature of 450 to 1,200 °C , preferably 500 to 900 °C .

A preferred method of exposing a copper chloride
5 etching waste liquor to a high-temperature atmosphere is to
sprinkle or spray the copper chloride etching waste liquor
into a high-temperature atmosphere.

It is desirable to previously concentrate the
copper chloride etching waste liquor to some degree in
10 order to improve the production efficiency of cupric oxide
and hydrogen chloride.

Hydrogen chloride, which is the other product
shown in the formula (3), is dissolved in water to collect
it as hydrochloric acid.

15 Fig. 3 is a flow diagram illustrating an
embodiment of the process of the present invention and an
embodiment of the apparatus of the present invention which
is suitable for the process embodiment. First a fixed
amount of a copper chloride etching waste liquor 1 which
20 has been discharged from a copper chloride etching
apparatus is fed to and is concentrated by a contact with a
high-temperature gas in a concentrating tower 2. A
preferred temperature of the high-temperature gas ranges
from 400 to 500 °C . The high-temperature gas used as the
25 heat source for the concentration is a gas mixture 3 which



1 has resulted by the removal of powdery cupric oxide 11 from
the hot decomposition product gas 11 generated in a
downstream roasting furnace 5. The water contained in the
copper chloride etching waste liquor 1 evaporates by the
5 direct, countercurrent contact of the gas mixture 3 with
the copper chloride etching waste liquor 1, and thus the
waste liquor 1 is concentrated. The gas mixture 3 is used
for the purpose of effective use of energy.

The concentrated copper chloride etching waste
10 liquor 4 is then discharged from the bottom of the
concentrating tower and is fed by the aid of, for example,
a feed pump to the roasting furnace 5. The roasting
furnace 5 as shown in Fig. 3 is a fluidized cylindrical
shaft roasting furnace, which is a preferred example of the
15 roasting furnace. The temperature in the roasting furnace
5 is preferably 450 to 1,200 °C, and it is more preferable
to control the temperature of the fluidized bed 23 in the
roasting furnace 5 to 500 to 900 °C with a hot blast. In
this embodiment, the hot blast is a hot combustion gas 8 of
20 a fuel, such as kerosene or propane gas, which has
generated in a hot blast furnace 7 and is blown into the
bottom portion of the roasting furnace 5. A gas
distribution plate 9 uniformizes the velocity
distribution of the combustion gas 8 to form a stable
25 fluidized bed 23 thereon. In the roasting furnace 5, in or



1 over the fluidized bed 23, the combustion gas 8 blown
upwardly through the gas distribution plate 9 comes into
contact with the droplets of the concentrated etching waste
liquor 4 which are sprinkled through an upper inlet of the
5 roasting furnace 5, and then the hydrochloric acid and
water in the droplets evaporate and, simultaneously, copper
chlorides are roasted and thermally oxidation-decomposed
into cupric oxide and hydrogen chloride. The resulting
fine particles of cupric oxide are discharged together with
10 the upward flow of the decomposition product gas through
the top portion of the roasting furnace 5. Reference
numeral 10 represents the decomposition product gas
discharged from the roasting furnace 5, which contains fine
particles of cupric oxide 11 and a gas mixture 3 containing
15 hydrogen chloride and vapor. A part of the generating
cupric oxide grows in the roasting furnace 5 into particles
of 0.5 to 5 mm in particle size, which form the fluidized
bed 23. A part of the particles forming the fluidized bed
23, however, are ground again into fine particles by the
20 friction due to their collision with each other and are
also discharged from the roasting furnace 5 in company with
the decomposition product gas. Excess particles forming
the fluidized bed 23 drop out of the roasting furnace 5
through a collecting outlet located higher than the gas
25 distribution plate 9.



1 The internal materials of the roasting furnace,
including those of the gas distribution plate, the
sprinkling nozzle and the internal furnace wall, should be
corrosion resistive.

5 Subsequently, the decomposition product gas 10
containing fine particles of cupric oxide, hydrogen
chloride and vapor is fed to a cyclone 12, where the
decomposition product gas 10 makes a spiral flow and
descends spirally in the cyclone 12, and most fine
10 particles of cupric oxide 11 are collected through the
lower end of the cyclone 12. The fine particles of cupric
oxide collected by the cyclone 12 generally are 50 μ m or
less in particle size.

 In a cooling tower 13, the remaining part of fine
15 particles of cupric oxide 11 and the gas mixture 3
containing hydrogen chloride and vapor are cooled to a
temperature of 400 to 500 °C at which electrostatic
precipitators are operable.

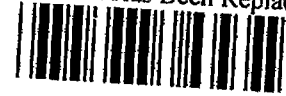
 After cooling in the cooling tower 13, the
20 remaining part of fine particles of cupric oxide 11 are
collected electrically in an electrostatic precipitator 14,
and the gas mixture 3 containing hydrogen chloride and
vapor is fed from the cooling tower 13 to the concentrating
tower 2. Almost all of cupric oxide close to 100 % can be
25 collected through the course from the roasting in the



1 roasting furnace 5 to the collection by the electrostatic
precipitator 14. The fine particles of cupric oxide
collected by the electrostatic precipitator 14 are
generally 0.5 to 50 μ m in particle size. Trace fine
5 particles of cupric oxide which have not been collected by
the electrostatic precipitator 14 do not cause any problem
since the fine particles accompany the gas mixture 3 to the
concentrating tower 2, where the fine particles are
dissolved in a fresh copper chloride etching waste liquor 1
10 and are then subjected again to roasting in the
roasting furnace 5.

The gas mixture 3 the heat of which has been
taken away in the concentrating tower 2 then flows into a
hydrochloric acid collecting tower 15, where hydrogen
15 chloride is dissolved in water 16 to collect it as
hydrochloric acid 17. An aqueous hydrochloric acid
solution of a concentration of 18 % or more can be obtained
in 98 % recovery or more by feeding pure water into the
hydrochloric acid collecting tower 15, with the partial
20 pressure of hydrogen chloride uniformalized.

An exhaust gas 18 containing remaining hydrogen
chloride and non-condensable gas is neutralized in a gas
cleaning tower 19 with an alkali solution 20, such as an
aqueous sodium hydroxide solution, and is then discharged
25 as a harmless waste liquor 21 and a harmless exhaust gas



1 22.

By using the process and apparatus for treating copper chloride etching waste liquor of the present invention, aqueous hydrochloric acid solution and cupric
5 oxide can be obtained in a percentage recovery close to 100 %, and the resultant aqueous hydrochloric acid may be reused circularly for the preparation of etchant, and the cupric oxide may be used effectively as a material for the production of printed wiring boards.

10 The technique of exposing the copper chloride etching waste liquor to a high-temperature atmosphere is not limited to the above-mentioned technique using a fluidized roasting furnace where a waste liquor is sprinkled or sprayed, and other common techniques, such as
15 the one using gas-liquid contacting plates with a large surface area, may also be used.

Although the above-described embodiment is for the treatment of the copper chloride etching waste liquor resulting from the etching process in the production of
20 printed wiring boards, the present invention can also be applied, for example, to the treatment of the copper chloride etching waste liquor which is generated in the production processes of copper clad laminates by treating the copper on the tag ends of copper clad laminates or on
25 defective copper clad laminates.



1 The fine particles of cupric oxide obtained by
the present invention are so fine that the fine particles
can be dissolved very easily in dissolution reagents.

 An example of the effective use of the resultant
5 cupric oxide is the production of copper clad laminate
which is a material of printed wiring boards. Copper clad
laminate is generally produced by laminating on a laminate
board an electrolytic copper foil formed from a copper
sulfate bath, in which the cupric oxide obtained by the
10 present invention may be used as a replenishing resource of
copper. The cupric oxide can also be used as a copper
resource for the copper sulfate bath which is used in the
electroplating process for the production of printed wiring
boards. Another method of making circuits of printed
15 wiring boards is an electroless copper plating method. The
electroless copper plating method is generally carried out
by forming a complex compound of copper with, for example,
ethylenediaminetetraacetic acid or sodium potassium
tartrate, adding thereto a reducing reagent, such as
20 formaldehyde, sodium hydrophosphite or glyoxylic acid, to
chemically deposit copper. The cupric oxide obtained by
the present invention can be used as a useful copper
replenishing resource because it forms easily such complex
compounds.

25 The cupric oxide obtained by the present



1 invention, further, may be used for producing
ultraconductors by mixing and roasting it with other rare
earth elements, or be compression sintered to form a powder
metallurgy product, or be reduced with hydrogen flame to
5 produce copper paste or a metal copper material.

The process of the present invention enables
efficient treatment of copper chloride etching waste
liquor, which has caused serious problems in the
environmental preservation, and as well enables recovery of
10 industrially useful materials from the waste liquor.
Examples of the effects of the present invention are as
follows:

- (1) Almost all of the hydrochloric acid resulting
from the thermal decomposition can be used for the
15 regeneration of copper chloride etchant, thereby enabling
the operation of a recycling system in one factory;
- (2) The treating process of the present invention is
more efficient, requires much less cost and is easier to
control, as compared with substitution method and
20 electrolytic method;
- (3) The resulting cupric oxide can be used
effectively as a copper material of good quality, for
example, for the production of electrolytic copper foil,
copper paste or ultraconductor, copper electroplating,
25 chemical plating or powder metallurgy.

1

EXAMPLE

5

20 kg of a copper chloride etching waste liquor was treated by the process of the present invention using a pilot plant of the apparatus as shown in Fig. 3.

First the copper chloride etching waste liquor was concentrated in a concentrating tower. The concentration was carried out by bringing the copper chloride etching waste liquor flowing in through the upper portion of the concentrating tower into contact with a hot gas mixture containing hydrogen chloride and vapor (the temperature of the gas mixture: 450°C), which had been generated by roasting a concentrated copper chloride etching waste liquor in a roasting furnace of a cylindrical shaft type, had been passed through a cyclone, a cooling tower and an electrostatic precipitator and was fed through the lower portion of the concentrating tower. The compositions of the copper chloride etching waste liquor and the concentrate thereof are shown in Table 1.

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Table 1

Components	Copper chloride etching waste liquor		Concentrated copper chloride etching waste liquor	
	%	kg	%	kg
CuCl ₂	21.20	4.24	40.00	4.43
CuCl	0.20	0.04	0	0
HCl	3.20	0.64	5.00	0.55
H ₂ O	75.40	15.08	55.00	6.09
Total	100.00	20.00	100.00	11.08

The concentrated copper chloride etching waste liquor was fed by a feed pump to the roasting furnace, where the fed etching waste liquor was sprinkled from an upper portion of the roasting furnace, while a combustion gas of kerosene was blown in through a gas distribution plate. The droplets of the concentrated copper chloride etching waste liquor came into contact with the combustion gas in the fluidized bed of the roasting furnace. The temperature of the fluidized bed was adjusted to 700 °C.

- 1 Table 2 shows the amounts of hydrogen chloride and vapor in
the gas mixture discharged from the roasting furnace.

Table 2

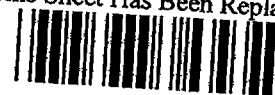
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Components	kg	Nm ³
HCl	2.96	1.82
H ₂ O	5.50	6.84
Total	8.46	8.65

10

- The cupric oxide generated by the roasting was
15 collected by using a cyclone, a cooling tower and an
electrostatic precipitator. In the cooling tower, the gas
mixture was cooled to 450 °C. Table 3 shows the
composition and the total yield of copper oxides which were
collected from the roasting furnace, the cyclone and the
20 electrostatic precipitator.

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Table 3

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Copper oxides		
Components	%	kg
CuO	99.50	2.62
Others	0.50	0.01
Total	100.00	2.63

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The particle sizes of the fine particles of cupric oxide collected from the roasting furnace, the cyclone and the electrostatic precipitator were 1 to 5mm, 1 to 100 μ m and 0.5 to 50 μ m, respectively.

The gas mixture discharged from the electrostatic precipitator was fed through the concentrating tower to a hydrochloric acid collecting tower, where the gas mixture was then brought into contact with 7.98 g in total of pure water. Table 4 shows the composition of the hydrochloric acid solution which flowed out from the hydrochloric acid collecting tower.





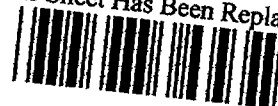
Table 4

Hydrochloric acid solution

Components	%	kg
HCl	18.00	2.96
H ₂ O	82.00	13.48
Total	100.00	16.44

As shown in Table 3 and Table 4, 2.62 kg of cupric oxide and 16.4 kg of a 18 % aqueous hydrochloric acid solution were obtained in a yield close to 100 %.

The obtained aqueous hydrochloric acid solution exhibited again its sufficient ability of regenerating a copper chloride etchant. The obtained cupric oxide had a very high purity of 99.5 % by weight. The relatively large particles of cupric oxide obtained in the roasting furnace and the cyclone were dissolved readily in an aqueous sulfuric acid solution to form a solution, which could be used as a mother liquid in copper sulfate electroplating and electrolytic copper foil plating without any problem. The ultra fine particles of cupric oxide obtained in the



1 electrostatic precipitator was dissolved sufficiently in a
sodium hydroxide · ethylenediaminetetraacetic acid solution
by using a stirring and mixing apparatus, and was then
filtered to remove solids, to form a mother liquid of an
5 electroless copper plating bath. Chemical plating of
copper on a printed board was confirmed by adding a
formaldehyde solution into the mother liquid which was kept
at 70 °C . Further, the obtained fine particles of cupric
oxide can also be used as a material of ultraconductor as
10 it is, or after washing with pure water followed by drying.
The obtained cupric oxide can also be reduced in a hydrogen
flame reduction furnace into powdery copper, to use as a
material of conductive copper paste, or can be used for
powder metallurgy by mixing and forming with other binders.

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1 What is claimed is,

1. A process for treating copper chloride etching waste liquor which generates in a process for etching copper with a copper chloride etchant, comprising: exposing said copper chloride etching waste liquor to an atmosphere of a high temperature ranging from 450 to 1,200 °C in the presence of oxygen to generate cupric oxide and hydrogen chloride, separating said cupric oxide and said hydrogen chloride, collecting the separated cupric oxide, dissolving the separated hydrogen chloride into water to form hydrochloric acid, and collecting said hydrochloric acid.

2. An apparatus for treating copper chloride etching waste liquor which generates in a process for etching copper with a copper chloride etchant, comprising:

(a) a roasting furnace for exposing said copper chloride etching waste liquor, which has been concentrated in a concentrating tower, to an atmosphere of a high temperature ranging from 450 to 1,200 °C, in the presence of oxygen, to generate cupric oxide and a gas mixture containing hydrogen chloride and vapor,

(b) a cyclone for separating and collecting said cupric oxide from said gas mixture,

(c) a cooling tower for cooling remaining cupric



1 oxide and said gas mixture which have been discharged from
the cyclone to a temperature of 400 to 500 °C ,

(d) an electrostatic precipitator for
electrically separating and collecting said remaining
5 cupric oxide from said gas mixture.

(e) a concentrating tower for concentrating
said copper chloride etching waste liquor by bringing said
copper chloride etching waste liquor into contact with said
gas mixture which has been discharged from said
10 electrostatic precipitator,

(f) a hydrochloric acid collecting tower for
bringing water into contact with said gas mixture which has
been discharged from the concentrating tower after the
contact with said copper chloride etching waste liquor, to
15 dissolve said hydrogen chloride contained in said gas
mixture into said water and to collect resulting
hydrochloric acid, and

(g) a gas cleaning tower for cleaning an exhaust
gas which has been discharged from said hydrochloric acid
20 collecting tower and contains remaining hydrogen chloride,
by neutralizing said exhaust gas with an aqueous alkali
solution.

