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Aeten Weaver

[NAME]

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(71) Applicant 000006183
 Mitsui Metals Mining Co., Ltd.
 1-11-1 Osaki, Shinagawa-ku, Tokyo
 (74) Agent: 100124327
 Attorney Katsuhiro Yoshimura
 (72) Inventor Mitsuyuki Matsuda
 1333-2 Haraichi, Ageo-shi, Saitama Prefecture
 Mitsui Mining & Smelting Co., Ltd. Research
 Institute
 (72) Inventor Hisao Sakai
 1333-2 Haraichi, Ageo-shi, Saitama Prefecture
 Mitsui Mining & Smelting Co., Ltd. Research
 Institute
 (72) Inventor Sakiko Tomonaga
 1333-2 Haraichi, Ageo-shi, Saitama Prefecture
 Mitsui Mining & Smelting Co., Ltd. Research
 Institute

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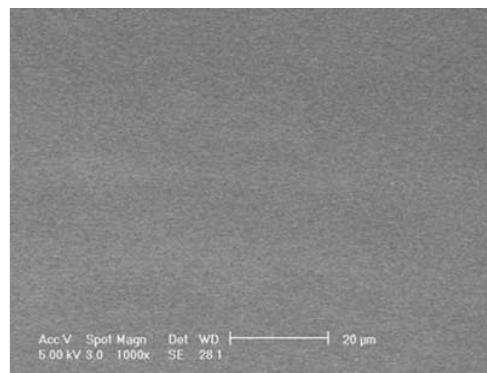
(54)[Name of Invention] Method of producing electrolytic copper foil and the electrolytic copper foil obtained by the manufacturing method, surface treated electrolytic copper foil obtained using the electrolytic copper foil, copper coated laminate plate and printed wiring plate using the surface treated electrolytic copper foil

(57) [Abstract]

[Challenges] Compared to the low-profile electrolytic copper foil that has been supplied to the conventional market, we will provide a shiny electrolytic copper foil with a lower profile.

[Solution means] In order to solve the above problem, the surface roughness (Rzjis) on the precipitation surface side is 1. The electrolytic copper foil has an ultra-low profile of less than $0\ \mu\text{m}$ and the gloss [Gs (60°)] of the precipitation surface is 400 or more. This electrolytic copper foil may then be electrolyzed using a sulfate-based copper electrolyte obtained by adding a quaternary ammonium salt polymer having a cyclic structure with 3-mercapto-1-propanesulfonic acid and/or bis(3-sulfopropyl) disulfide and chlorine.

[Representative drawing] Fig. 1



[Scope of patent claims]

[Claim 1]

The surface roughness (Rzjis) of the precipitation surface side is 1. Electrolytic copper foil characterized by less than $0\ \mu\text{m}$ and a gloss [Gs (60°)] of 400 or greater.

[Claim 2]

The gloss [Gs (60°)] of the precipitation surface side is measured in the cross direction and the ratio of the TD gloss to the MD gloss measured in the machine direction ([TD gloss] / [MD gloss]) is 0.9 - 1.1.

[Claim 3]

Electrolytic copper foil according to claim 1 or claim 2, characterized in that the precipitation surface side comprises a relationship between gloss [Gs (20°)] > gloss [Gs (60°)].

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[Claim 4]

The glossy side has a surface roughness (Rzjis) of 2. The electrolytic copper foil according to any of Claims 1 to 3, characterized in that it is less than $0\ \mu\text{m}$ and has a gloss [Gs (60°)] of 70 or more.

[Claim 5]

The electrolytic copper foil according to any of Claims 1 to 4, wherein the tensile strength in normal conditions is 33 kgf/mm² or more and the elongation is 5% or more.

[Claim 6]

The electrolytic copper foil according to any of Claims 1 to 5, wherein the tensile strength after heating (180°C × 60 minutes, atmosphere) is 30 kgf/mm² or more, and the elongation after heating (180°C × 60 minutes, atmosphere) is 8% or more.

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[Claim 7]

The electrolytic copper foil according to claim 1, wherein the surface of the electrolytic copper foil is subjected to at least one of an antirust treatment and a silane coupling agent treatment.

[Claim 8]

The method of claim 1, wherein the surface roughness (Rzjis) of the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil is 1. The surface treated electrolytic copper foil of claim 7, characterized in that it is $5\ \mu\text{m}$ or less.

[Claim 9]

The surface treated electrolytic copper foil of claim 7 or claim 8, characterized in that the gloss [Gs (60°)] of the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil is 250 or more.

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[Claim 10]

The surface-treated electrolytic copper foil of claim 7, characterized in that the surface-treated electrolytic copper foil has been roughened on the adhesive surface side with the insulating layer construction material.

[Claim 11]

The surface treated electrolytic copper foil according to any of Claims 7 to 10, characterized in that the adhesive surface of the surface treated electrolytic copper foil with the insulating layer construction material is a precipitation surface.

[Claim 12]

Method of stripping copper precipitated on a cathode surface by an electrolytic method using a sulfate-based copper electrolyte to produce an electrolytic copper foil, the method comprising:

Method for producing an electrolytic copper foil characterized in that the sulfate-based copper electrolyte comprises a quaternary ammonium salt polymer having a cyclic structure with at least one selected from 3-mercapto-1-propanesulfonic acid or bis(3-sulfopropyl)disulfide.

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[Claim 13]

A total concentration of 3-mercapto-1-propanesulfonic acid and/or bis(3-sulfopropyl)disulfide in the sulfate-based copper electrolyte is 0. The method for producing electrolytic copper foil according to claim 12, characterized in that it is between 5 ppm and 100 ppm.

[Claim 14]

Method for producing electrolytic copper foil according to Claim 12 or Claim 13, characterized in that the concentration of quaternary ammonium salt polymer having a cyclic structure in the sulfate-based copper electrolyte is 1 ppm to 150 ppm

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[Claim 15]

Method for producing electrodeposited copper foil according to any of claims 12 to 14, characterized in that the quaternary ammonium salt polymer having a cyclic structure in the sulfuric acid-based copper electrolyte is a diallyldimethylammonium chloride polymer.

[Claim 16]

Method for producing electrolytic copper foil according to any of Claims 12 to 15, characterized in that the chlorine concentration in the sulfate-based copper electrolyte is between 5 ppm and 120 ppm.

[Claim 17]

Electrolytic copper foil manufactured by the manufacturing method of claim 12.

[Claim 18]

A copper-coated laminate plate in which the surface treated electrolytic copper foil of any of Claims 7 to 11 is clung to the insulating layer component material.

[Claim 19]

The rigid copper-clad laminate of claim 18, wherein the insulating layer construction material contains skeletal material.

[Claim 20]

Rigid printed wiring board characterized in that it was obtained using a rigid copper cladding laminate according to claim 19.

[Claim 21]

The flexible copper-clad laminate according to claim 18, wherein the insulating layer construction material is composed of flexible material having flexibility.

[Claim 22]

A flexible printed wiring board characterized in that it was obtained using the flexible copper-clad laminate according to claim 21.

[Detailed Description of the Invention]

[Technical field]

[0001]

The present invention relates to a method for producing electrolytic copper foil, surface-treated electrolytic copper foil, electrolytic copper foil, a copper-clad laminate plate using the surface-treated electrolytic copper foil, and a printed wiring plate. In particular, it relates to an electrolytic copper foil having a low profile and high gloss on the mating surface with the insulating layer construction material of the electrolytic copper foil.

[Background Technology]

[0002]

Because metallic copper is a favorable conductor of electricity, relatively inexpensive and easy to handle, electrolytic copper foil is widely used as the foundation material for printed wiring boards. In addition, for electronic and electrical equipment, where printed wiring boards are often used, it is necessary to reduce the size and weight, etc., so-called light, thin, and small. In the past, in order to achieve such light, thin, and small electronic and electrical equipment, it is necessary to make the signal circuits as finely pitched as possible, and manufacturers, etc. have responded by adopting thinner copper foil to reduce the time set for over-etching when forming the wiring by etching, and by improving the etch factor of the forming wiring.

[0003]

In addition, demands for enhanced functionality are also being made for electronic and electrical equipment that is miniaturized and lightened. Therefore, in order to ensure the largest possible part mounting area within the limited substrate area due to the spread of surface mounting methods, it has been necessary to take measures to improve the etch factor of the wiring of the printed wiring board. For this purpose, in particular, tape automatic bonding (TAB) substrates and chip-on-film (COF) substrates, which are so-called interposer substrates that are mounted directly on IC chips, etc., have been required to have low-profile electrolytic copper foil that is more than normal printed wiring board applications. It should be noted that the profile refers to the surface roughness R_{zj} , which is the tangential interface with the insulating layer-forming material in the standards for copper foil for printed wiring boards (the application for this matter will be used without using [the tangential interface] and will be referred to as [the tangential interface]).

It is defined by the value measured in the TD direction according to 601-2001, and low profile means that the surface roughness Rz of the adhesive surface is small.

[0004]

In order to solve such problems, Patent Reference 1 discloses a surface treated electrolytic copper foil characterized in that the surface roughness Rz of the precipitation surface of the untreated electrolytic copper foil is the same as or smaller than the surface roughness Rz of the gloss surface of the untreated electrolytic copper foil, and the adhesive surface is treated with a roughening treatment on the precipitation surface of the foil. In addition, the above-mentioned untreated electrolytic copper foil is manufactured using an electrolytic solution with a compound having a mercapto group, a chloride ion, a low molecular weight gutter with a molecular weight of 10,000 or less, and a polymeric polysaccharide. Specifically, the compounds having the mercapto group are 3-mercapto 1-propanesulfonate, the molecular weight of the low molecular weight gut is 3000 or less, and the polymeric polysaccharide is hydroxyethyl cellulose.

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[0005]

In addition, Patent Reference 2 discloses a method for producing electrolytic copper foil that is characterized by the use of an electrolytic copper plating solution containing a copolymer of diallyl dialkylammonium salt and sulfur dioxide in a method for producing electrolytic copper foil by electrolysis of an acidic copper plating solution of sulfate. The acid sulfate copper plating solution concerned should contain polyethylene glycol, chlorine and 3-mercapto-1-sulfonic acid. The roughness of the precipitation surface used as the adhesive surface with the insulating substrate is small, and the average roughness Rz of 10 points is $1.0 \mu\text{m} \pm 0$. It is said that a low profile of about $5 \mu\text{m}$ can be obtained.

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And when these manufacturing methods are used to produce electrolytic copper foil, a low profile precipitation surface is certainly formed, and it has favorable characteristics as a conventional low profile electrolytic copper foil.

[0007]

[Patent Reference 1] JP 9-143785 Publication

[Patent Reference 2] JP 2004-35918 Publication

[Disclosure of the invention]

[Problem to be solved by the invention]

[0008]

On the other hand, the clock frequency of personal computers, which are representative of electronic or electrical equipment, is increasing, and the computing speed is exponentially faster. In the past, not only data processing, which is the original role of a computer, but also functions that use the computer itself in the same way as an AV device have been added. In other words, not only the music playback function, but also the DVD recording playback function, T V image reception recording function, and video telephone function are added one after another.

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[0009]

In other words, it is not enough to simply satisfy the data monitoring function of a personal computer monitor, and image quality is required to withstand long-term viewing even when viewing images such as movies, etc. And it is necessary to supply such quality monitors inexpensively and in large quantities. The current monitor uses a large number of liquid crystal monitors, and it is common to use the aforementioned tape automatic bonding (TAB) substrate and chip-on-film (COF) substrate to mount the driver element of this liquid crystal panel. In addition, in order to achieve high definition of the monitor, the driver board also needs to form a finer circuit to meet the increase in the number of scan lines. In addition, efforts are being made to reduce product dimensions by making the outer edge as narrow as possible as the panel size increases. In order to place the driver on the back, it was necessary to install the TAB substrate or COF substrate by folding, and from the beginning, it was also required to have favorable flexibility. In the COF, unlike TAB, the bonded lead portion is lined with film. Therefore, it is disadvantageous in terms of flexibility compared to TAB without film, and the use of materials with better flexibility than before is effective in preventing breakage.

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[0010]

On the other hand, with the spread of hybridization and the development of fuel cell cars in electronic circuits for automotive use, large electric currents are being compelled. The conductor thickness required for automotive applications will continue to be 2

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It is used as a flexible wiring board from a space saving perspective, despite the speculation that it exceeds $00\ \mu\text{m}$. In order to apply such thick copper foil to a flexible substrate, it is essential that the adhesive surface roughness of the copper foil is small, and rolled copper foil is also being considered as being unable to be handled with conventional electrolytic copper foil. That is, in the case of conventional electrolytic copper foil, the thicker the thickness, the larger the adhesive surface roughness with the substrate.

[0011]

It is also preferable to use a copper foil with a smooth surface when used as a negative electrode current collector for a lithium ion battery. In other words, when applying active materials on copper foil, it is advantageous to use a copper foil with a smooth surface as a current collector in order to coat a slurry containing active materials on copper foil with uniform coating thickness. In addition, because the negative electrode active material in question repeatedly expands and deflates during charging and discharging, there is also a large change in the size of copper foil as a current collector material, and the expansion and deflation cannot follow the expansion and deflation behavior of copper foil, resulting in a phenomenon of breaking. Thus, the mechanical properties of the copper foil, which is a current collector, withstand repeated expansion and contraction behavior, so a favorable balance of tensile strength and elongation is required. Furthermore, it is equally advantageous to use a smooth surface copper foil when forming a dielectric layer for capacitors on copper foil by sol-gel method.

[0012]

As described above, the market has been expanding for electrolytic copper foil due to the use of printed wiring boards. As a result, it became clear that there was a demand for electrolytic copper foil with a lower profile at a thickness of $450\ \mu\text{m}$ or less and favorable flexibility compared to the low profile electrolytic copper foil for printed wiring board applications that have been supplied to the conventional market.

[Means for Solving the Problems]

[0013]

Based on the above background, the present inventors conceived of low-profile electrolytic copper foil having productivity that is not inferior to conventional electrolytic copper foil production technology, and with a maximum thickness that can be accommodated exceeding $450\ \mu\text{m}$.

[0014]

Electrolytic copper foil according to the present invention: The present invention has a surface roughness (R_{zjs}) of 1. The electrolytic copper foil is provided that is less than $0\ \mu\text{m}$ and has a gloss [$G_s(60^\circ)$] of 400 or greater on the precipitation surface.

[0015]

In the electrolytic copper foil incorporated into the present invention, the ratio of the gloss [$G_s(60^\circ)$] on the precipitation surface side measured in the width direction to the gloss [$[(TD\ gloss)/(MD\ gloss)]$] measured in the flow direction is 0.9 - 1. It is preferably 1.

[0016]

In addition, in the electrolytic copper foil incorporated into the present invention, it is preferable that the precipitation surface side comprises a relationship between gloss [$G_s(20^\circ)$] > gloss [$G_s(60^\circ)$].

[0017]

Furthermore, in the electrolytic copper foil incorporated into the present invention, the glossy surface side has a surface roughness (R_{zjs}) of 2. Preferably, it is less than $0\ \mu\text{m}$ and has a gloss [$G_s(60^\circ)$] of 70 or greater.

[0018]

From the perspective of the mechanical properties of the electrolytic copper foil incorporated into the present invention, the electrolytic copper foil exhibits mechanical properties with a tensile strength of $33\ \text{kgf/mm}^2$ or more and an elongation rate of 5% or more in normal conditions.

[0019]

In addition, the electrolytic copper foil incorporated into the present invention exhibits mechanical properties with a tensile strength of $30\ \text{kgf/mm}^2$ or more after heating ($180^\circ\text{C} \times 60\ \text{minutes}$, atmosphere) and an elongation rate of 8% or more after heating ($180^\circ\text{C} \times 60\ \text{minutes}$, atmosphere).

[0020]

Surface treated electrolytic copper foil incorporated into the present invention: The surface-treated electrolytic copper foil incorporated into the present invention is one or more of rust-prevention treatment or silane coupling agent treatment on the surface of the electrolytic copper foil described above.

Yeah.

[0021]

In addition, the surface roughness (Rzjis) of the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil incorporated into the present invention is 1. It is preferably 5 μm or less.

[0022]

In addition, it is preferable to use a surface treated electrolytic copper foil with a gloss [Gs (60°)] of 250 or more as the adhesive surface with the insulating layer construction material according to the present invention.

[0023]

In addition, it is preferred that the surface treated electrolytic copper foil incorporated into the present invention be roughened on the adhesive surface side of the surface treated electrolytic copper foil with the insulating layer component material.

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[0024]

In addition, it is preferable to use the precipitation surface of the above-mentioned electrolytic copper foil as the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil incorporated into the present invention.

[0025]

Methods of producing electrolytic copper foil incorporated into the present invention: The method for producing the electrolytic copper foil incorporated into the present invention is characterized by a method of stripping copper deposited on the cathode surface by electrolytic method using a sulfate-based copper electrolyte, wherein the sulfate-based copper electrolyte comprises a quaternary ammonium salt polymer and chlorine having a cyclic structure with at least one type selected from 3-mercapto-1-propanesulfonic acid (hereinafter referred to as [MPS] in the present application) or bis(3-sulfopropyl) disulfide (hereinafter referred to as [SPS] in the present application).

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[0026]

The method of claim 1, wherein the combined concentration of MPS and/or SPS in the sulfate-based copper electrolyte is 0. It is preferable to use between 5 ppm and 100 ppm.

[0027]

It is desirable that the concentration of the quaternary ammonium salt polymer having a cyclic structure in the sulfate-based copper electrolyte is between 1 ppm and 150 ppm.

[0028]

In addition, it is particularly preferred to use a diallyl dimethylammonium chloride (hereinafter referred to as "DDAC" in the present application)) polymer as a quaternary ammonium salt polymer having a cyclic structure.

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[0029]

In addition, the chlorine concentration in said sulfate-based copper electrolyte is preferably between 5 ppm and 120 ppm.

[0030]

The present invention provides an electrolytic copper foil manufactured by the aforementioned manufacturing method.

[0031]

Copper-clad laminate according to the present invention: The copper-clad laminate according to the present invention is obtained by covering the surface treated electrolytic copper foil and insulating layer construction material. In addition, in the case where the insulating layer component material comprising the copper-clad laminate according to the present invention contains skeletal material, it is a rigid copper-clad laminate. On the other hand, in the case where the insulating layer construction material comprising the copper-clad laminate according to the present invention is a flexible material having flexibility, it is a flexible copper-clad laminate.

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[0032]

Printed Wiring Boards for the Invention: A copper-clad laminate can be obtained using the surface treated electrolytic copper foil incorporated into the present invention, and by etching this copper-clad laminate, a printed wiring plate according to the present invention can be obtained. That is, a rigid printed wiring board can be obtained by using the rigid copper cladding laminate described above. In addition, flexible printed wiring boards can be obtained by using the flexible copper-clad laminate mentioned above.

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[Effect of the Invention]

[0033]

The electrolytic copper foil incorporated into the present invention has even better low-profile characteristics compared to

the low-profile electrolytic copper foil products conventionally supplied to the market. As a result, the electrolytic copper foil incorporated into the present invention has superior gloss over conventional low profile electrolytic copper foil. Furthermore, the electrolytic copper foil incorporated into the present invention is pronounced to be low profile as the thickness increases as electrolytic copper foil. This trend is the opposite of conventional electrolytic copper foil products, which profile higher with increasing thickness.

[0034]

In addition, when this electrolytic copper foil is actually supplied to the market, various surface treatments are applied to prevent oxidation due to atmosphere and improve adhesion to the substrate, and are generally supplied as surface treated electrolytic copper foil. By using the electrolytic copper foil incorporated into the present invention, it is possible to achieve a low profile that exceeds the low profile electrolytic copper foil applied to the market even if the surface treatment is performed as long as such surface treatment is performed properly.

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[0035]

Therefore, when the surface-treated electrolytic copper foil incorporated into the present invention is used in a copper-coated laminated plate, the thickness uniformity of the insulating layer located between the conductor layers composed of the surface-treated electrolytic copper foil incorporated into the present invention is excellent, and even when a thin insulating layer is used, the insulation reliability between the layers is dramatically improved without causing a short circuit. In particular, a uniform roughening process makes it suitable for high frequency copper coated laminates.

[0036]

Furthermore, the printed wiring board obtained by etching the copper coated laminate according to the present invention is suitable for the formation of fine pitch circuits because it is possible to reduce the profile of the surface treated electrolytic copper foil incorporated into the present invention used in the copper coated laminate.

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[Best Embodiments of the Invention]

[0037]

[Form of electrolytic copper foil incorporated into the present invention]

Before explaining the electrolytic copper foil incorporated into the present invention, we will state the general method for producing electrolytic copper foil so that it is easier to understand the explanation. [Electrolytic copper foil] pertaining to the present invention is a condition in which no surface treatment has been performed, and it may be referred to as [untreated copper foil], [segregation and separation foil], etc. In the present specification, this is simply referred to as [electrolytic copper foil]. The production of this electrolytic copper foil generally employs a continuous production method, in which a sulfate-based copper electrolyte is flowed between a rotating cathode in a drum shape and a lead-based anode or a dimensionally stable anode (DSA) disposed oppositely along the shape of the rotating cathode, and the copper is precipitated onto the surface of the rotating cathode using an electrolytic reaction, and this precipitated copper is continuously peeled away from the rotating cathode as a foil state and wound. Since the electrolytic copper foil obtained in this way is a roll wound at a constant width, the rotational direction of the rotating cathode (length direction of the web) is referred to as the MD (Machine Direction) and the transverse direction of the width direction perpendicular to the MD is referred to as the TD (Transverse Direction).

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[0038]

The surface shape of the side peeled off from the state in contact with the rotating cathode of this electrolytic copper foil has been referred to as the "gloss surface" because the shape of the polished rotating cathode surface has a gloss. On the other hand, the surface shape on the side that was the precipitation side shows the uneven shape of the peak shape because the crystal growth rate of copper that normally precipitates varies from crystal surface to surface, and this side is referred to as the "precipitation surface." In general, the roughness of the precipitation surface is greater than the roughness of the glossy surface, and when surface treatment is applied to the electrolytic copper foil, the roughening treatment is often applied to the precipitation surface side, and this precipitation surface side becomes the mating surface with the insulating layer component material when producing the copper-clad laminate. Thus, the smaller the surface roughness of this adhesive surface, the better the low profile surface treated electrolytic copper foil.

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[0039]

In this way, the electrolytic copper foil is subjected to a surface treatment such as roughening treatment and oxidation prevention to reinforce the adhesion of the insulating layer component material with a mechanical anchoring effect, and the electrolytic copper foil that distributes the market is completed, but it may be used without roughening treatment depending on the application. Next, the electrolytic copper foil incorporated into the present invention is described below.

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[0040]

The electrolytic copper foil incorporated into the present invention has a surface roughness (Rzjis) of 1. Less than $0\ \mu\text{m}$ and with a gloss [Gs (60°)] of 400 or more. More preferably, surface roughness (Rzjis) is 0. Less than $6\ \mu\text{m}$, gloss [Gs (60°)] is greater than 600. First, we will explain the gloss. Here, the gloss of [Gs (60°)] is a measurement of the intensity of light irradiated to the surface of the electrolytic copper foil at an incident angle of 60° and bounced back at a reflection angle of 60°. The angle of incidence referred to here is 0°, which is the perpendicular direction to the surface irradiated with light. In addition, according to JIS Z 8741-1997, five mirror gloss measurement methods with different angles of incidence are described, and it is said that the optimal angle of incidence should be selected according to the gloss of the sample. Among other things, it is said that by setting the angle of incidence to 60°, it is possible to measure a wide range of samples from low gloss to high gloss. Therefore, 60° was mainly used for the gloss measurement of electrolytic copper foil, etc., according to the present invention.

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[0041]

In general, surface roughness Rzjis has been used as a parameter to evaluate the smoothness of the precipitated surface of electrolytic copper foil. However, Rzjis alone can only obtain uneven information in the height direction, and cannot obtain information such as uneven cycles or undulations. Because gloss is a parameter that reflects the information of both, various parameters such as the roughness cycle of the surface, undulation, and uniformity within those surfaces can be determined together when used in conjunction with Rzjis.

[0042]

In the case of electrolytic copper foil incorporated into the present invention, the surface roughness (Rzjis) on the precipitation surface side is 1. It is less than $0\ \mu\text{m}$ and the gloss [Gs (60°)] of the precipitation surface is 400 or greater. In other words, electrolytic copper foil that can guarantee quality within such a range and that can be supplied to the market did not exist in the past. By using the manufacturing method described below appropriately, the surface roughness (Rzjis) is 0. Less than $6\ \mu\text{m}$, the gloss [Gs (60°)] can also provide electrolytic copper foil with more than 700 precipitation surfaces. In addition, although there is no upper limit for gloss, it is limited to about 780 at [Gs (60°)] based on empirical judgment. The glossiness in the present invention was measured using a glossometer VG-2000 model manufactured by Nihon Denko Co., Ltd. in accordance with JISZ 8741-1997, which is a method of measuring the glossiness.

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[0043]

And with regard to the electrolytic copper foil products mentioned here, there are no limitations on the thickness. This is because the thicker the precipitation surface, the smaller the roughness and the higher the gloss. If the upper limit is set, it is targeted at electrolytic copper foil with a thickness of $450\ \mu\text{m}$ or less, which is a limit that can be profitable even when industrially manufacturing electrolytic copper foil.

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[0044]

Also, the lower limit of surface roughness (Rzjis) on the precipitation surface side is not limited here. The lower limit of surface roughness is empirically 0. It is about $1\ \mu\text{m}$. However, in the actual measurement, variation is seen, and the lower limit as a guaranteed measurement value is 0. It is considered to be about $2\ \mu\text{m}$.

[0045]

In addition, the electrolytic copper foil incorporated into the present invention takes the gloss [Gs (60°)] on the side of the precipitation surface divided into the TD gloss measured in the width direction and the MD gloss measured in the flow direction, and when this ratio ([TD gloss] / [MD gloss]) is taken, it is 0.9 - 1. It is in the range of 1. This means that the difference between the width direction and the flow direction is very small.

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[0046]

In other words, it was common knowledge that electrolytic copper foil has different mechanical properties between the width direction (TD) and the flow direction (MD) due to the influence of abrasive streaks, etc., on the surface of the rotating drum which is a cathode. However, the electrolytic copper foil incorporated into the present invention has a more uniform and smooth surface on the precipitation surface regardless of thickness, and the gloss [Gs (60°)] as its appearance is a value of [TD gloss] / [MD gloss] of 0.9 - 1.1, and the change width is within 10%, meaning that the surface shape variation between the TD direction and the MD direction of the electrolytic copper foil pertaining to the present invention is extremely small.

[0047]

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Furthermore, the fact that there is no difference in appearance in the TD direction and MD direction means that uniform electrolysis is performed, and even in the crystal structure, it is uniform. That is, it means that the difference in mechanical properties such as tensile strength and elongation rate will also be reduced depending on the TD direction and MD direction. If the difference in mechanical properties between the TD direction and the MD direction is thus small, the effect of the direction of copper foil on the substrate dimensional change rate and circuit linearity, etc. when manufacturing the printed wiring board is small and preferred. Incidentally, in the case of rolled copper foil, which can be said to be representative of copper foil having a smooth surface, it is widely known that the mechanical properties of the TD direction and the MD direction differ due to the processing method. As a result, the film carrier tape market, which is the application envisioned by the present invention, and thin rigid printed wiring boards, etc., have a large dimensional change rate, and it has been evaluated that they are not suitable for fine pattern applications.

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[0048]

By using [Gs (20°)] and [Gs (60°)] as gloss, the difference between conventional low-profile electrolytic copper foil can be more clearly seen. Specifically, the electrolytic copper foil incorporated into the present invention can have a relationship between the aforementioned precipitation surface [Gs (20°)] > [Gs (60°)] The same material is expected to be sufficient to evaluate the glossiness by selecting one angle of incidence, but since the reflectance varies depending on the angle of incidence, if the angle of incidence changes, the spatial distribution of reflected light changes depending on the irregularities of the surface of the measured surface, resulting in a difference in gloss. Based on these facts, the inventors, etc. in this case examined the results, and found that there was an empirical tendency to: That is, in the case of high-gloss and low-surface roughness electrolytic copper foil, a relationship between gloss [Gs (20°)] > gloss [Gs (60°)] > gloss [Gs (85°)] is established, and in the case of low-gloss and low-surface roughness electrolytic copper foil, a relationship between gloss [Gs (60°)] > gloss [Gs (20°)] > gloss [Gs (85°)] is established. Furthermore, in the case of electrolytic copper foil products with no gloss and low surface roughness, the relationship between gloss [Gs (85°)] > gloss [Gs (60°)] > gloss [Gs (20°)] is established. As can be seen above, in addition to the absolute value of gloss at a constant angle of incidence, it is meaningful to evaluate smoothness by relation to gloss measurements at different angles of incidence.

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[0049]

In the case of electrolytic copper foil incorporated into the present invention, the surface condition of the gloss surface is also important. This gloss surface requires surface roughness (Rzjis) and gloss [Gs (60°)] at levels close to the precipitation surface of the electrolytic copper foil incorporated into the present invention. That is, in the electrolytic copper foil incorporated into the present invention, the gloss surface side has a surface roughness (Rzjis) of 2. Preferably, it is less than $0\ \mu\text{m}$ and has a gloss [Gs (60°)] of 70 or greater. More preferably, the surface roughness (Rzjis) is 1. It is desirable to have a gloss [Gs (60°)] of less than $7\ \mu\text{m}$ and greater than 100. The upper limit of the gloss [Gs (60°)] is not specified, but empirically it is at 500. That is, in order to obtain the surface condition of the precipitation surface described so far, it is preferable to form a surface condition as described herein on the glossy surface. If this condition is removed, it is likely that the surface conditions will differ in the TD direction and MD direction, and it is also likely that mechanical property differences such as tensile strength and elongation rate will occur in the TD direction and MD direction. The surface condition of this shiny surface is a transcription of the surface condition of the cathode, which is the electrodeposition surface, and is determined by the surface condition of the cathode. Therefore, especially when producing thin electrolytic copper foil, the surface roughness (Rzjis) of the cathode surface is 2. Characterization of less than $0\ \mu\text{m}$ is required.

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[0050]

As for the mechanical properties of the electrolytic copper foil incorporated into the present invention, the tensile strength under normal conditions is $33\ \text{kgf/mm}^2$ or more, and the elongation rate is 5% or more. Preferably, after heating ($180^\circ\text{C} \times 60$ minutes, atmospheric atmosphere), the tensile strength is $30\ \text{kgf/mm}^2$ or more, and the elongation is 8% or more.

[0051]

In addition, in the present invention, by optimizing the manufacturing conditions, it is possible to have superior mechanical properties such as a normal tensile strength of $38\ \text{kgf/mm}^2$ or more and a tensile strength of $33\ \text{kgf/mm}^2$ or more after heating ($180^\circ\text{C} \times 60$ minutes, atmosphere). Thus, this favorable mechanical property may be sufficiently resistant to the folding use of flexible printed circuit boards.

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It is also suitable for use in current collection materials that constitute a negative electrode, such as a lithium ion secondary battery that undergoes expansion and contraction behavior.

[0052]

[Form of surface treated electrolytic copper foil incorporated into the present invention]

The surface-treated electrolytic copper foil incorporated into the present invention provides surface-treated electrolytic copper foil that has undergone one or more of rust prevention treatment or silane coupling agent treatment on the surface of the electrolytic copper foil described above. This rust-prevention treatment layer is intended to prevent oxidative corrosion of the surface of the electrolytic copper foil so as not to interfere with the manufacturing process of the copper-clad laminate and printed wiring boards. It is then recommended that the configuration be improved if possible without inhibiting adhesion to the insulating layer component material. The method used for the rust prevention treatment is not problematic even if organic rust prevention using benzotriazole, imidazole, etc., or inorganic rust prevention using zinc, chromate, zinc alloy, etc., or both are used in combination.

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[0053]

The silane coupling agent treatment is a treatment to chemically improve adhesion with the insulating layer component material after the rust prevention treatment has ended.

[0054]

Next, methods of forming a rust-prevention treatment layer will be described. In the case of organic rust prevention, it is possible to form the organic rust prevention agent solution by immersion application, shower ring application, electroplating method, etc. In the case of inorganic rust prevention, it is possible to use a method of electrolytically exposing rust prevention elements onto the surface of electrolytic copper foil, other so-called displacement precipitation methods, etc. For example, when zinc rust prevention treatment is performed, zinc pyrophosphate galvanized bath, zinc cyanide galvanized bath, zinc sulfate galvanized bath, etc. can be used. For example, in a galvanized pyrophosphate bath, the concentration is zinc 5 g/l to 30 g/l, potassium pyrophosphate 50 g/l to 500 g/l, liquid temperature 20°C to 50°C, pH 9 to 12, current density 0.3A/dm² to 10A/dm².

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[0055]

In addition, the silane coupling agent used in the above-mentioned silane coupling agent treatment is not particularly limited, and it is possible to optionally use epoxy-based silane coupling agent, amino-based silane coupling agent, mercapto-based silane coupling agent, etc., taking into account the properties of the insulating layer construction material used, plating liquid used in the printed wiring plate manufacturing process, etc. In addition, silane coupling agent treatment can be performed by employing methods such as immersion application of a solution of silane coupling agent, shower ring application, electroposition, and the like.

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[0056]

More specifically, it is possible to use coupling agents similar to those used in glass cloth of prepregs for printed wiring boards, such as vinyltrimethoxysilane, vinylphenyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, 4-glycidylbutyltrimethoxysilane, γ -aminopropyltriethoxysilane, N- β -(aminoethyl) γ -aminopropyltrimethoxysilane, N-3-(4-(3-aminopropoxy) butoxy) propyl-3-aminopropyltrimethoxysilane, imidazole silane, triazine silane, and γ -mercaptopropyltrimethoxysilane.

[0057]

The surface roughness (Rzjis) of the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil is 1. Preferably, it has a low profile of 5 μ m or less. Surface roughness is adjusted to this range, making it a surface treated copper foil suitable for forming fine pitch circuits.

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[0058]

It is also preferred that the gloss [Gs (60°)] of the adhesive surface of the surface treated electrolytic copper foil with the insulating layer construction material is 250 or greater. Because surface treatment forms a rust-prevention coating or a silane coupling agent coating, even at levels where no changes in surface roughness are detected, it is conceivable that the reflectance of light, etc. will change in comparison before and after surface treatment. Thus, although the absolute value of gloss may vary after surface treatment, the gloss obtained at the bonding surface of the surface treated electrolytic copper foil [

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If the Gs (60°) is maintained above 250, it can be determined that the surface treated coating is formed at the proper thickness.

[0059]

It is also preferred that the surface treated electrolytic copper foil is subjected to a roughening treatment on the adhesive surface with the insulating layer construction material. The roughening treatment can be applied to known technologies, and it is sufficient to perform the minimum necessary roughening treatment based on the combination with the rust prevention technology. However, in the formation of fine pitch wiring such that the surface treated electrolytic copper foil incorporated into the present invention is preferably less than the 25 μm pitch used, it is preferable to increase the accuracy of the over-etching time required.

[0060]

In addition, as a method of roughening, either a fine metal grain is adhered to the surface of the electrolytic copper foil, or a roughening surface is formed by an etching method is employed. Here, as a method of depositing the former fine metal grains, a method of depositing the copper fine grains onto a surface is illustrated. This roughening process consists of precipitating and depositing fine copper particles on the surface of the electrolytic copper foil, and over-plating steps to prevent this fine copper particle from falling out.

[0061]

In the process of precipitating and adhering fine copper particles onto the surface of the electrolytic copper foil, the conditions of stake plating are adopted as the electrolytic conditions. Therefore, in general, the solution concentration used in the process of precipitating and depositing fine copper granules is low so that it is easy to create a smear plating condition. This smudge plating condition is not particularly limited, but is determined in consideration of the characteristics of the production line. For example, if copper sulfate-based solutions are used, the concentration is 5 to 20 g/l copper, 50 to 200 g/l free sulfate, other additives as necessary (α -naphthoquinoline, dextrin, gutter, thiourea, etc.), the liquid temperature is 15 to 40°C, and the current density is 10 to 50 A/dm².

[0062]

In addition, the coating plating process to prevent the dropping of fine copper grains is a process to uniformly precipitate copper so that the fine copper grains are coated according to smooth plating conditions. Thus, a copper electrolyte similar to that used in the aforementioned electrolytic copper foil manufacturing process can be used here as a source of copper ions. This smooth plating condition is not particularly limited, but is determined in consideration of the characteristics of the production line. For example, if a copper sulfate-based solution is used, the concentration is 50 to 80 g/l copper, 50 to 150 g/l free sulfuric acid, the liquid temperature is 40 to 50°C, and the current density is 10 to 50 A/dm².

[0063]

In addition, it is said that the adhesive surface of the surface treated electrolytic copper foil with the insulating layer construction material is preferably on the precipitation surface side. As mentioned above, it is difficult to eliminate any difference in the TD direction/MD direction because the surface shape of the cathodic drum is a transferred shape. Therefore, it is preferable to use the precipitation surface side as the adhesive surface in order to minimize the linearity variation of the wiring end surface that occurs when the shape of the adhesive surface has direction in TD/MD.

[0064]

[Form of the method for producing electrolytic copper foil incorporated into the present invention]

The present invention provides a method of producing an electrolytic copper foil by peeling off copper precipitated on a cathode surface by an electrolytic method using a sulfate-based copper electrolyte, the sulfate-based copper electrolyte comprising a quaternary ammonium salt polymer having a cyclic structure with at least one type selected from MPS or SPS and chlorine. By using this composition of sulfate-based copper electrolyte, it is possible to manufacture electrolytic copper foil with a low profile according to the present invention stably. Furthermore, by optimizing the electrolytic conditions, the gloss [Gs (60°)] can be obtained as well as more than 700. The copper concentration in this sulfate-based copper electrolyte is 40 g/l to 120 g/l, the more preferred range is 50 g/l to 80 g/l, the free sulfuric acid concentration is 60 g/l to 220 g/l, and the more preferred range is 80 g/l to 150 g/l.

[0065]

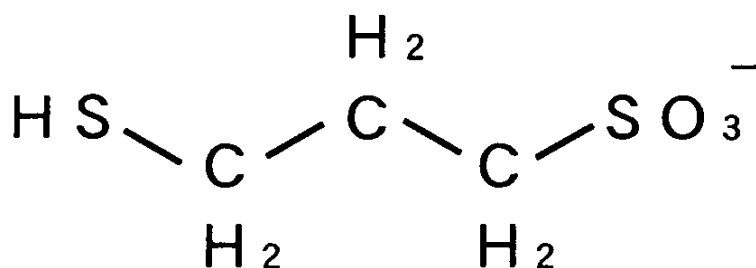
The combined concentration of MPS and/or SPS in the sulfate-based copper electrolyte according to the present invention is 0.5 ppm

It is preferably 100 ppm, more preferably 0.5 ppm to 50 ppm, more preferably 1 ppm to 30 ppm. The concentration of this MPS or SPS is 0. When less than 5 ppm, the precipitation surface of the electrolytic copper foil becomes rough, making it difficult to obtain a low profile electrolytic copper foil. On the other hand, even if the concentration of MPS and/or SPS exceeds 100 ppm, the effect of smoothing the precipitation surface of the resulting electrolytic copper foil does not improve, and only increases the cost of waste treatment. Furthermore, MPS and/or SPS as described in the present invention are used in the sense that each salt is also included, and the stated value of concentration is the equivalent value of sodium 3-mercapto-1-propanesulfonate as a sodium salt (hereinafter referred to as "MPS-Na" in the present application]. In addition, MPS adopts an SPS structure by dimerizing in the sulfate-based copper electrolyte according to the present invention, and therefore, the concentration of MPS or SPS is the concentration that includes 3-mercapto-1-propanesulfonic acid alone, salts such as MPS-Na added as SPS, and denatures polymerized into SPS, etc. after addition to the electrolyte as MPS. The following shows the structural formula of MPS as Clarification 1 and the structural formula of SPS as Clarification 2. The comparison of these structural formulas shows that the SPS structure is a binary of the MPS.

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[0066]

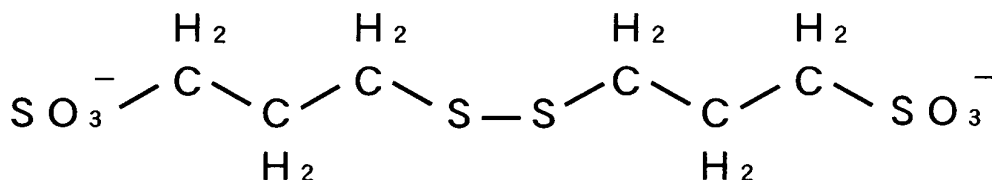
[Reaction 1]



[0067]

[Reaction 2]

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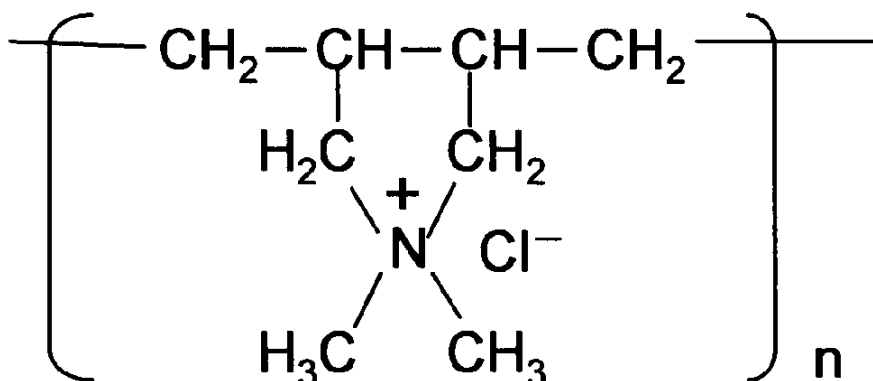
[0068]

In addition, the quaternary ammonium salt polymer having a cyclic structure in the sulfate-based copper electrolyte according to the present invention preferably has a concentration of 1 ppm to 150 ppm, more preferably 10 ppm to 120 ppm, and even more preferably 15 ppm to 40 ppm. Here, a variety of quaternary ammonium salt polymers having a cyclic structure can be used, but most preferably DDAC polymers are used given the effect of forming a low profile precipitation surface. DDACs form a cyclic structure when taking the polymer structure, and some of the cyclic structure will consist of nitrogen atoms of quaternary ammonium. Since the DDAC polymer is believed to be either a 4-membered ring to a 7-membered ring or a mixture thereof, the compound taking the 5-membered ring structure of these polymers is represented here, and is shown below as Reaction 3. This DDAC polymer is a polymer structure in which the DDAC has more than a dimer, as is evident in Reaction 3.

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[0069]

[Reaction 3]



[0070]

The concentration in the sulfate-based copper electrolyte of this DDAC polymer is preferably between 1 ppm and 150 ppm, more preferably between 10 ppm and 120 ppm, and even more preferably between 15 ppm and 40 ppm. When the concentration of DDAC polymer in the sulfuric acid copper electrolyte is less than 1 ppm, no matter how much the concentration of MPS or SPS is increased, the deposited copper surface becomes rough, making it difficult to obtain low-profile electrolytic copper foil. Even if the concentration in the sulfate-based copper electrolyte of the DDAC polymer exceeds 150 ppm, the precipitation state of copper becomes unstable, making it difficult to obtain low-profile electrolytic copper foil.

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[0071]

Further, the chlorine concentration in the sulfate-based copper electrolyte is preferably between 5 ppm and 120 ppm, and more preferably between 10 ppm and 60 ppm. If this chlorine concentration is less than 5 ppm, the precipitation surface of the electrolytic copper foil becomes coarse and the low profile cannot be maintained. On the other hand, when the chlorine concentration exceeds 120 ppm, the precipitation surface of the electrolytic copper foil becomes rougher, the electrocrystallization state becomes unstable, and the precipitation surface with a low profile cannot be formed.

[0072]

As described above, the component balance between the MPS or SPS in the sulfate-based copper electrolyte and the DDAC polymer and the chlorine is most important, and if these quantitative balances deviate from the above range, the precipitation surface of the electrolytic copper foil will become coarse and it will not be possible to maintain a low profile.

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[0073]

In addition, in the case of the electrolytic copper foil being manufactured using the sulfate-based copper electrolyte, the electrolytic is performed using a cathodic and insoluble anode with a surface roughness adjusted to the desired range. It is recommended that the liquid temperature be between 20°C and 60°C, more preferably between 40°C and 55°C, the current density be between 15A/dm² and 90A/dm², more preferably between 50A/dm² and 70A/dm².

[0074]

In addition, in the case of the method of manufacturing the electrolytic copper foil incorporated into the present invention, in order to obtain the properties required for the electrolytic copper foil described above stably, the cathode surface condition should also be managed when manufacturing the same. Referring to JIS C 6515, which is the standard for electrolytic copper foil for printed wiring boards, the surface roughness (Rzjis) of the glossy surface required for electrolytic copper foil is at most 2. It is specified to be 4 μm. The cathode used in the manufacture of this electrolytic copper foil is a rotating cathode drum made of titanium (Ti) material, and changes in appearance and metal phase due to surface oxidation occur during continuous use. Therefore, a mechanical machining operation of regular surface polish, polishing or cutting is required depending on the condition. Such mechanical processing of the cathode surface is performed while rotating the cathode, so a circumferentially muscular processing pattern inevitably occurs. Therefore, it is difficult to maintain the surface roughness (Rzjis) at steady state while remaining small, and the aforementioned standard values are allowed on the premise that they do not interfere with the manufacturing of printed wiring boards from a cost perspective.

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[0075]

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In the case of conventional electrolytic copper foil, the thicker the precipitation surface roughness tends to increase, and it is understood empirically that electrolytic copper foil obtained using a cathode drum having an upper limit level or higher of the aforementioned general standard value tends to increase the surface roughness of the precipitation surface due to the influence of the surface shape of the cathode. On the other hand, when the electrolytic copper foil incorporated into the present invention is manufactured, the above-mentioned copper sulfate-based electrolytic solution is used to reduce the effect of the cathode surface shape and enable the formation of flat precipitation surfaces in the process of thickening while filling the irregularities of the cathode surface. Therefore, even using a somewhat coarse cathode of the surface is less susceptible to the shape of the cathode surface, such as conventional electrolytic copper foil. In addition, as long as the manufacturing method described herein is adopted, the thicker the electrolytic copper foil, the more flat the precipitation surface the electrolytic copper foil is obtained.

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[0076]

However, in electrolytic copper foil products with a thickness of less than $20\ \mu\text{m}$, its precipitation surface roughness (Rzjis) is 1. If less than $0\ \mu\text{m}$, the roughness of the glossy surface of the resulting electrolytic copper foil is 2. Less than $0\ \mu\text{m}$, preferably 1. Using a cathode in a surface state that can be less than $2\ \mu\text{m}$, gloss [Gs (60°)] preferably 70 or greater and 120 or greater is preferred from the perspective of reducing the difference in mechanical and surface properties in the TD direction and MD direction as described above.

[0077]

The present invention provides an electrolytic copper foil manufactured by the aforementioned manufacturing method.

[0078]

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[Form of copper-clad laminate according to the present invention]

The present invention provides a copper-clad laminate of said surface-treated electrolytic copper foil to be clung to an insulating layer construction material. With regard to the manufacturing method of these copper-clad laminates, it is possible to use the conventional method of roll laminate or casting method for flexible copper-clad laminates, and it is possible to manufacture rigid copper-clad laminates using a hot press or continuous laminate method. It should be noted that the flexible copper-clad laminate and rigid copper-clad laminate described in the present invention are concepts that include all of a single-sided copper-clad laminate, a double-sided copper-clad laminate, and a multi-layer copper-clad laminate. Here, in the case of a multi-layer copper-clad laminate, the surface treated copper foil according to the present invention is used as the outer layer, and the inner layer comprises an inner layer core material comprising an inner layer circuit. In the following description of the copper coated laminate, there is no explanation to distinguish between them. This is because it will be duplicated.

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[0079]

The present invention provides a rigid copper cladding laminate in which the insulating layer construction material contains skeletal material. It has been reported that the majority of the skeletal materials used in conventional rigid copper-clad laminates are glass woven or non-woven, and the roughness of the copper foil adhesive surface affects interlayer insulation at levels above $10\ \mu\text{m}$, and migration resistance due to direct contact between the glass fiber, which is the skeletal material, and the circuit even at $10\ \mu\text{m}$ or less can be problematic. At the $5\ \mu\text{m}$ level, it was said that there was no cause for concern. However, in recent years, for example, BGA and CSP, which are package substrates that are directly mounted with electronic components, have also been required to have a fine pattern that has not been conventionally done, and the surface has been flattened by using aramid fibers thinner than glass fibers as skeletal material in nonwoven fabric. Furthermore, when components, etc., with higher clock frequencies are installed, the transmission characteristics of the signal in the high frequency range are not satisfied when the linearity and cross-sectional shape of the circuit are far from the ideal state. Therefore, the copper-clad laminate according to the present invention is suitable for the manufacturing application of printed wiring boards having transmission circuits of high frequency signals, not only fine patterns.

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[0080]

In addition, the present invention provides a flexible copper-clad laminate plate composed of flexible materials that are flexible in the insulating layer construction materials described above. Flexible copper-clad laminates have been separated from rigid copper-clad laminates in terms of flexibility and light weight, and insulating layer materials have been made thinner to achieve light weight and high flexibility. At the same time, thinning is also required for the conductor layer, and electrolytic copper foil is the main material. In addition, in order to ensure insulation reliability in thin films, especially in multilayer flexible substrate applications, a low profile of less than 1/10 of the thickness of the insulating layer is required for the adhesive surface, so if it is a conventional product, the above surface roughness

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Rzjis = 5 μm was the upper limit of use. However, the flexible copper-clad laminate using the electrolytic copper foil of the present invention can ensure insulation reliability even if the film thickness is further reduced. In addition, it has superior flexibility compared to the flexible copper-clad laminate using conventional low-profile electrolytic copper foil, and it is also a copper-clad laminate with improved reliability in this regard.

[0081]

Here, a method for producing rigid copper-clad laminates and flexible copper-clad laminates is specifically illustrated. When making rigid copper-clad laminate or flexible copper-clad laminate, a flexible insulating layer forming material such as surface treated electrolytic copper foil, FR-4 class prepreg, etc., or polyimide resin film, etc., or mirror plate, according to the present invention, is used to form the desired lay-up state, and is pressed between 170°C and 200°C.

[0082]

On the other hand, in the case of a flexible copper-clad laminate, it is possible to adopt the roll laminate method and casting method as described above. This roll laminate method is a method of thermal crimping at the pressure of a heating roll using a roll of surface treated copper foil according to the present invention and a roll of resin film such as polyimide resin film and PET film. The casting method is to form a resin composition film that becomes polyimide resin by heating polyamic acid, etc., on the surface of the surface treated copper foil according to the present invention, and directly form a polyimide resin film on the surface of the surface treated copper foil by heating to cause a condensation reaction.

[0083]

[Form of printed wiring board according to the present invention]

In addition, the present invention provides a rigid printed wiring board characterized in that it was obtained using the aforementioned rigid copper-clad laminate. As described above, in the manufacture of printed wiring boards using the copper-clad laminate using the electrolytic copper foil with a smooth adhesive surface according to the present invention, not only the subtractive method but also the pattern plating/flash etching method can be used, and in either case, the overetching time can be set to a short time, so that the end faces of the obtained circuit are straighter and the cross section is closer to a rectangle. Therefore, it is a printed wiring board with excellent overall reliability, with excellent insulation reliability between circuits in a fine pattern, excellent signal transmission characteristics in high frequency regions flowing near the circuit surface due to the skin effect, and also resistant to noise such as crosstalk.

[0084]

In addition, the present invention provides a flexible printed wiring board characterized in that it was obtained using the aforementioned flexible copper-clad laminate. In manufacturing this printed wiring board, like the rigid printed wiring board described above, not only the subtractive method but also the pattern plating/flash etching method can be used. In either case, the overetching time can be set to a short time, so that the end faces of the obtained circuit are straighter and the cross section is closer to a rectangular shape. Therefore, it is a printed wiring board with excellent reliability and excellent signal transmission characteristics in high frequency regions, and it also does not generate noise such as crosstalk, and at the same time it has excellent insulation reliability and flexibility, and it is capable of demonstrating its advantage especially when it is a film carrier that directly mounts parts.

[0085]

Here, the above rigid copper-clad laminate or flexible copper-clad laminate (hereinafter referred to as simply "copper-clad laminate".) An example of a common processing method when machining a printed circuit board using any of the , is described for the avoidance of doubt. First, an etch resist layer is formed on the surface of the copper-clad laminate, the etch circuit pattern is exposed, developed, and an etch resist pattern is formed. The etch resist layer at this time is made of photosensitive resins such as dry film and liquid resist. In addition, UV exposure is common for exposure, and a method of forming an etch resist pattern based on a routine method can be employed.

[0086]

Then, by etching the electrolytic copper foil into a circuit shape using a copper etchant, and performing an etch resist peeling, the desired circuit shape is

formed. With regard to etchants at this time, all copper etchants such as acidic copper etchants and alkaline copper etchants can be used.

[0087]

As described above, the copper-clad laminate according to the present invention is described as a concept that includes all of a single-sided copper-clad laminate, a double-sided copper-clad laminate, and a multilayer copper-clad laminate with an inner layer circuit. Therefore, in the case of a double-sided copper-clad laminate and a multi-layer copper-clad laminate, it may be necessary to ensure continuity between the layers, and in such cases, through holes, via holes, etc. are formed according to the standard method, and then continuity plating is performed to obtain interlayer continuity. Generally, this conductive plating process involves performing activation treatment using a palladium catalyst, followed by electroless copper plating, and then growing the film thickness by electrolytic copper plating.

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[0088]

When copper etching is completed, water washing is performed sufficiently, and rust prevention treatment, etc. is performed as necessary, such as drying, to become rigid printed wiring board or flexible printed wiring board.

[Examples of embodiments]

[0089]

Considering that the surface shape of the cathode does not affect the example compared to the example, the surface is polished with 2000 polishing paper, and the surface roughness is reduced to 0. Titanium plate electrodes adjusted to 85 μm were used.

[0090]

[Embodiment Group 1]

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In this Embodiment Group 1, Embodiments 1 to 8 were implemented. In Embodiments 1 to 8, a copper sulfate solution having a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, and an MPS concentration, a DDAC polymer (Unisense FP A100L, manufactured by Senka Corporation), and a chlorine concentration as shown in Table 1 were used as the sulfuric acid-based copper electrolytic solution. In Embodiment 9, SPS, which is a binary of MPS, was used as an alternative to MPS.

[0091]

[Table 1]

Subject	Additive concentration (ppm)		
	MPS-Na	DDAC polymer	Chlorine
Embodiment 1	5	3	10
Embodiment 2	5	3	10
Embodiment 3	7	5	10
Embodiment 4	7	5	10
Embodiment 5	4	3	10
Embodiment 6	4	3	10
Embodiment 7	21	20	10
Embodiment 8	21	20	10
Embodiment 9	7*	5	10
*: The MPS-Na concentration in Embodiment 9 is the equivalent value when SPS is used as Na salt			

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[0092]

For the creation of electrolytic copper foil, DSA was used for the anode, electrolyzed at a liquid temperature of 50°C and current density of 60A/dm² to obtain nine electrolytic copper foil products of 12 μm and 210 μm thickness. The mechanical properties of the copper foil were evaluated only in this 12 μm electrolytic copper foil. The results are shown in Table 2.

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[0093]

[Table 2]

	Copper Foil Thickness (μm)	Electrolytic copper foil physical properties			
		Normal		After heating ($180^{\circ}\text{C} \times 60 \text{ min.}$)	
		Tensile strength (kgf/mm^2)	Growth rate (%)	Tensile strength (kgf/mm^2)	Growth rate (%)
Embodiment 1	12	38.2	6.2	34.6	9.8
Embodiment 3	12	36.6	8.2	32.9	10.3
Embodiment 5	12	39.3	8.1	34.3	11.0
Embodiment 7	12	35.3	7.7	31.7	10.5
Embodiment 9	12	36.7	7.9	32.2	11.0
Comparative Example 1	12	36.2	4.0	32.4	5.6
Comparative Example 2	12	31.4	3.5	26.8	5.8
Comparative Example 3	12	40.5	3.6	39.5	4.4
Comparative Example 4	12	38.6	4.0	37.4	4.8

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[0094]

The electrolytic copper foil was then subjected to rust prevention treatment on both sides. Here, inorganic rust prevention under the following conditions was adopted. A zinc sulfate bath was used to set the free sulfuric acid concentration at 70 g/l and the zinc concentration at 20 g/l, the liquid temperature was 40°C , the current density was 15 A/dm^2 , and zinc anti-rust treatment was performed.

[0095]

Further, in the present embodiment, a chromate layer was formed electrolytically over the zinc rust-prevention layer. The electrolytic conditions at this time are as follows: chromic acid concentration 5.0 g/l, pH 11.5, liquid temperature 35°C , current density 8 A/dm^2 , electrolysis time 5 seconds.

[0096]

After the rust prevention treatment was completed as described above, the silane coupling agent was immediately adsorbed on the rust prevention treatment layer on the precipitation surface in a silane coupling agent treatment tank. The solution composition at this time was γ -glycidoxypolytrimethoxysilane concentration of 5 g/l using pure water as the solvent. This solution was then adsorbed by spraying with a shower ring.

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[0097]

Upon completion of the silane coupling agent treatment, the moisture was eventually dissipated by an electrothermal device to obtain nine types of surface treated electrolytic copper foil. According to the crystal structure analysis of the electrolytic copper foil obtained, the average crystal particle size was larger than the average crystal particle size of the electrolytic copper foil with a low profile due to the fine crystallization used in conventional film carrier tapes, and the presence of twin crystals was also confirmed. The surface roughness (R_{zjis}) and gloss [$\text{Gs}(20^{\circ})$], [$\text{Gs}(60^{\circ})$] and [$\text{Gs}(85^{\circ})$] of the deposit side of the electrolytic copper foil obtained above, and the surface roughness (R_{zjis}) and gloss [$\text{Gs}(60^{\circ})$] of the deposit side of the surface-treated electrodeposited copper foil are shown in Table 3.

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[Table 3]

	Copper Foil Thickness (μm)	Electrolytic copper foil								Surface treated copper foil		
		Precipitation surface								Precipitation surface		
		Rzjis (μm)	Gloss							Rzjis (μm)	Gloss	
			Gs (20°)		Gs (60°)			Gs (85°)			Gs (60°)	
			TD	MD	TD	MD	TD/MD	TD	MD		TD	MD
Embodiment 1	12	0.30	844	988	652	675	0.97	129	138	0.32	621	647
Embodiment 2	210	0.27	1169	1263	624	661	0.94	124	129	0.33	592	602
Embodiment 3	12	0.33	910	970	647	673	0.96	129	140	0.29	597	613
Embodiment 4	210	0.29	1074	1144	656	670	0.98	115	128	0.36	546	547
Embodiment 5	12	0.35	718	838	643	660	0.97	123	138	0.33	581	602
Embodiment 6	210	0.34	1147	1182	631	662	0.95	112	119	0.36	587	582
Embodiment 7	12	0.33	941	1043	650	677	0.96	132	142	0.30	606	611
Embodiment 8	210	0.30	1223	1271	661	692	0.96	118	124	0.32	576	576
Embodiment 9	12	0.34	800	824	650	674	0.96	117	133	0.32	618	623
Comparative Example 1	12	0.85	-	-	-	283	-	-	-	-	-	-
	210	0.70	-	-	-	221	-	-	-	-	-	-
Comparative Example 2	12	0.83	-	-	-	374	-	-	-	-	-	-
	210	1.22	-	-	-	386	-	-	-	-	-	-
Comparative Example 3	12	3.60	-	-	-	0.7	-	-	-	-	-	-
Comparative Example 4	12	3.59	-	-	-	1.0	-	-	-	-	-	-

[0098]

[Embodiment Group 2]

Here, Embodiments 10 to 14 used a solution adjusted to a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, and a concentration of SPS as described in Table 4, a DDAC polymer (unisense FPA 100 L made of Senka (strain)), and a chlorine concentration as sulfate-based copper electrolyte.

[0099]

[Table 4]

	Additive concentration (ppm)		
	SPS-Na	DDAC polymer	Chlorine
Example 10	5	30	25
Example 11	10	20	22
Example 12	100	100	100
Example 13	50	70	100
Example 14	50	100	50

[0100]

The creation of electrolytic copper foil was electrolyzed using a DSA on the anode at a liquid temperature of 50°C and a current density of 60 A/dm², and two electrolytic copper foil products of 12 μm and 70 μm thickness were obtained in Example 10 and four electrolytic copper foil products of 12 μm thickness were obtained in Examples 11-14.

[0101]

The normal state of the 12 μm and 70 μm electrolytic copper foil obtained in Example 10 and 180°C x 60 min. The tensile strength and elongation rate after heating are shown in Table 5. The tensile strength of the 12 μm electrolytic copper foil in question is 35. 5 kgf/mm², growth rate 11. 5%, 180°C x 60 min. The tensile strength after heating is 33. 2 kgf/mm², 11. The favorable mechanical properties of 2% are at levels that are sufficient to withstand the folding use of flexible printed circuit boards.

[0102]

[Table 5]

	Copper Foil Thickness (μm)	Normal		180°C × 60 min. After heating	
		Tensile strength	Growth Rate	Tensile strength	Growth Rate
		Kgf/mm ²	%	Kgf/mm ²	%
Embodiment 10	12	35.5	11.5	33.2	11.2
	70	34.4	28.0	32.3	31.8
Comparative Example 5	12	37.9	8.0	31.6	7.5

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[0103]

When evaluating the fold resistance of the above 12 μm electrolytic copper foil alone by MIT method, it is able to withstand folding tests of 1,200 to 1,350 times and 800 to 900 times even after heating. The fold resistance test according to the above MIT method uses a film fold resistance test machine with tank made by Toyo Seiki Corporation (part number: 549) as the MIT fold resistance device, and the bending radius is 0.8 mm, load 0.5 kgf and sample size 15 mm x 150 mm. This number is approximately 600 times normal when evaluating general-purpose electrolytic copper foil used in conventional flexible printed wiring board applications under the same conditions, and 500 times after heating, so it shows approximately twice the fold resistance of conventional general-purpose products. It can be inferred that this difference is due to the effect that the smooth surface is less likely to cause cracks that can lead to fracture.

[0104]

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Then, the electrolytic copper foil obtained above was immersed in a dilute sulfuric acid solution at a concentration of 150 g/l and a liquid temperature of 30°C for 30 seconds, and the deposits and surface oxidative film were removed and washed with water. For the 12 μm electrolytic copper foil and 70 μm electrolytic copper foil obtained in Example 10, a total of four types of surface treated electrolytic copper foil and two types of surface treated electrolytic copper foil without roughening were created, respectively.

[0105]

The 12 μm electrolytic copper foil and 70 μm electrolytic copper foil that are subject to roughening treatment above were subjected to the process of precipitation and deposition of fine copper particles on the precipitation surface as a process of forming fine copper particles on the precipitation surface of the electrolytic copper foil when the acid washing process is completed, and the coating process was applied to prevent the dropping of these fine copper particles. In the process of precipitating and adhering the fine copper grains of the former, a copper sulfate-based solution was electrolyzed for 5 seconds under the conditions of copper concentration 15 g/l, free sulfuric acid concentration 100 g/l, liquid temperature 25°C, and current density 30 A/dm².

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[0106]

When fine copper particles were adhered to the precipitation surface, copper was evenly precipitated to cover the fine copper particles under smooth plating conditions as a coating plating process to prevent the removal of the fine copper particles. Here, as the smooth plating conditions, copper sulfate solution was set to a copper concentration of 60 g/l, free sulfuric acid concentration of 100 g/l, liquid temperature of 45°C, current density of 45 A/dm², and electrolyzed for 5 seconds.

[0107]

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In this example, rust prevention treatment was performed on both sides of all electrolytic copper foil obtained, and inorganic rust prevention was adopted in this case under the conditions described below. A zinc sulfate bath was used to set the free sulfuric acid concentration at 70 g/l and the zinc concentration at 20 g/l, the liquid temperature was 40°C, the current density was 15 A/dm², and zinc anti-rust treatment was performed.

[0108]

The chromate layer was further electrolytically formed over the zinc rust prevention layer. The electrolytic conditions at this time are as follows: chromic acid concentration 5.0 g/l, pH 11.5, liquid temperature 35°C, current density 8 A/dm², electrolysis time 5 seconds.

[0109]

After the rust prevention treatment was completed as described above, the silane coupling agent was immediately adsorbed on the rust prevention treatment layer on the precipitation surface in a silane coupling agent treatment tank. The solution composition at this time was such that pure water was used as a solvent and the concentration of γ -glycidioxypropyltrimethoxysilane was

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5 g/l. This solution was then adsorbed by spraying with a shower ring. When the silane coupling agent treatment was finished, the water was eventually dissipated by an electrothermal device to obtain six types of surface treated electrolytic copper foil, including one type of roughening treatment foil.

[0110]

Table 6 shows the surface roughness (Rzjis) and gloss [Gs (60°)] on the glossy side of the electrolytic copper foil obtained from Examples 10-14 above, the surface roughness (Gs (20°)) and gloss [Gs (60°)] on the precipitated side, [Gs (60°)] and [Gs (85°)], and the surface roughness (Gs (60°)) on the precipitated surface of the surface treated foil obtained from Example 10, and the surface roughened surface roughened surface (Rzjis).

[0111]

[Table 6]

	Copper Foil Thickness (μm)	Electrolytic copper foil											Surface treated copper foil			
		Glossy surface			Precipitation surface								Precipitation surface			Roughening surface Rzjis (μm)
		Gloss Gs (60°)		Rzjis (μm)	Gloss Gs (20°)		Gloss Gs (60°)			Gloss Gs (85°)		Rzjis (μm)	Gloss Gs (60°)		Rzjis (μm)	
		TD	MD		TD	MD	TD	MD	TD/MD	TD	MD		TD	MD		
Embodiment 10	12	165	311	0.87	1027	1058	659	665	0.99	142	139	0.32	540	514	0.28	0.97
	70	140	291	0.84	1510	1506	691	686	1.01	149	150	0.17	570	570	0.15	-
Example 11	12	157	294	1.14	925	1206	735	759	0.97	114	112	0.30	-	-	-	-
Example 12	12	158	279	0.91	823	976	613	651	0.94	98	118	0.39	-	-	-	-
Example 13	12	159	295	0.97	800	955	603	665	0.91	116	129	0.41	-	-	-	-
Example 14	12	158	295	1.02	867	968	627	649	0.97	114	129	0.32	-	-	-	-
Comparative Example 1	12	150	260	1.14	116	126	324	383	0.85	111	117	1.00	150	260	0.98	1.70

[Comparative Example]

[0112]

[Comparative Example 1]

This comparative example is the trace experiment of Example 1 described in Patent Reference 2. As a sulfate-based copper electrolyte, the basic solution was dissolved in pure water with copper sulfate (reagent) and sulfuric acid (reagent), and the concentration of copper sulfate (5-hydrate conversion) was 280 g/l, and the concentration of free sulfuric acid was 90 g/l. Then, the copolymer of diallyl dialkylammonium salt and sulfur dioxide (brand name PAS-A-5, weight average molecular weight 4000) was adjusted to 4 ppm, polyethylene glycol (average molecular weight 1000) to 10 ppm, and MPS-Na to 1 ppm, and furthermore, sodium chloride was used to prepare a chlorine concentration of 20 ppm as an acidic copper sulfate plating solution.

[0113]

The anode was electrolyzed using a lead plate at a liquid temperature of 40°C and a current density of 50 A/dm² to obtain electrolyzed copper foils of 12 μm and 210 μm thickness. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and gloss [Gs (60°)] of the precipitate surface are shown in Table 3, along with examples.

[0114]

[Comparative Example 2]

In this comparative example, a solution with a copper concentration of 90 g/l and a free sulfuric acid concentration of 110 g/l was cleaned through an activated carbon filter as a sulfate-based copper electrolyte. Copper electrolytes were then added to this solution so that the concentration of MPS-Na was 1 ppm, the concentration of hydroxyethylcellulose was 5 ppm, the concentration of low molecular weight gut (number average molecular weight 1560) was 4 ppm, and the concentration of chlorine was 30 ppm as polymeric polysaccharides. Using the copper electrolyte prepared in this manner, electrolysis was performed using a DSA electrode on the anode at a liquid temperature of 58°C and a current density of 50 A/dm² to obtain electrolytic copper foil products with a thickness of 12 μm and 210 μm. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and glossiness of the precipitated surface, etc., are shown in Table 3 together with the examples.

[0115]

[Comparative Example 3]

In this comparative example, the sulfuric acid-based copper electrolyte had a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, a DDAC polymer (Unisense FPA100L, manufactured by Senka Corporation) concentration of 4 ppm, and

A solution with a prime concentration of 15 ppm was used. The anode was electrolyzed with a DSA electrode at a liquid temperature of 50°C and a current density of 60 A/dm² to obtain an electrolytic copper foil with a thickness of 12 μm. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and glossiness of the precipitated surface, etc., are shown in Table 3 together with the examples.

[0116]

[Comparative Example 4]

In this comparative example, the sulfuric acid-based copper electrolyte used had a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, a DDAC polymer (Unisense FPA100L, manufactured by Senka Corporation) concentration of 4 ppm, a low molecular weight glue (number average molecular weight 1560) concentration of 6 ppm, and a chlorine concentration of 15 ppm. The anode was electrolyzed with a DSA electrode at a liquid temperature of 50°C and a current density of 60 A/dm² to obtain an electrolytic copper foil with a thickness of 12 μm. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and gloss [Gs (60°)] of the precipitate surface are shown in Table 3, along with examples.

[0117]

[Comparative Example 5]

This comparative example is the trace experiment of Embodiment 1 described in Patent Reference 2. The basic solution of the sulfate-based copper electrolyte was dissolved in pure water with copper sulfate (reagent) and sulfuric acid (reagent), and the concentration of copper sulfate (5-hydrate conversion) was 280 g/l, and the concentration of free sulfuric acid was 90 g/l. This was adjusted to 4 ppm for the copolymer (manufactured by Nitto Tosei Co., Ltd., trade name PAS-A-5, weight average molecular weight 4000), 10 ppm for the polyethylene glycol (average molecular weight 1000), and 1 ppm for the MPS-Na concentration, and 20 ppm for the chlorine concentration using sodium chloride.

[0118]

The anode was electrolyzed using a lead plate at a liquid temperature of 40°C and a current density of 50 A/dm² to obtain electrolyzed copper foil with a thickness of 12 μm and 70 μm, and then two types of surface-treated electrolyzed copper foil were obtained in the same manner as Example 10. The normal state of this electrolytic copper foil and 180°C × 60 min. The mechanical properties after heating are shown in Table 5, and the surface roughness (Rzjis), gloss [Gs (20°)], [Gs (60°)], and [Gs (85°)], surface roughness (Rzjis) and gloss [Gs (60°)], and roughening surface (Rzjis) of the roughening treated foil are shown in Table 6.

[0119]

[Comparison with Embodiments and Comparative Examples]

Each comparative example and embodiment will be compared and the results will be described below. The precipitation surface side of the electrolytic copper foil obtained in the example is surface roughness (Rzjis) < 1.0 μm, gloss [Gs (60°)] ≥ 400 and its TD/MD ratio is 0.9 - 1.1 and [Gs (20°)] > [Gs (60°)] > [Gs (85°)] In addition, the mechanical properties of normal conditions meet the conditions of the present invention, with the tensile strength of 33 kgf/mm² or higher having an elongation rate of 5% or more, and the mechanical properties after heating having a tensile strength of 30 kgf/mm² or higher having an elongation rate of 8% or more.

[0120]

Comparative to Comparative Example 1: Comparatively comparing the surface roughness (Rzjis) of the precipitation surface side of the electrolytic copper foil, the electrolytic copper foil of Comparative Example 1 also has a favorable low profile. However, the surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil incorporated into the present invention is 0.30 μm to 0. The surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil in Comparative Example 1 was 0. The surface roughness (Rzjis) of the precipitation surface of 85 μm and 210 μm electrolytic copper foil incorporated into the present invention is 0.27 μm to 0. The surface roughness (Rzjis) of the precipitation surface of the 210 μm electrolytic copper foil in Comparative Example 1 is 0. It is 70 μm. Therefore, while there is a common tendency for a smoother precipitation surface to be obtained as the copper foil thickness increases, the electrolytic copper foil incorporated into the present invention is superior in the absolute value of smoothness. Also, when comparing the gloss [Gs (60°)], the gloss [Gs (60°)] of Comparative Example 1 is in the range of 221 to 283, whereas the gloss [Gs (60°)] of each example shows a completely different range of 603 to 759. Based on this, compared to the electrolytic copper foil of Comparative Example 1, it can be said that each electrolytic copper foil of the Example has a flatter, closer precipitation surface to the mirror surface. As for the mechanical properties,

the 12 μm electrodeposited copper foil of Comparative Example 1 had a tensile strength of 36.2 kgf/mm², elongation rate 4.0%, tensile strength after heating 32.4 kgf/mm², 5.6%, which is equivalent to the electrolytic copper foil of the example is the tensile strength in normal conditions.

[0121]

Comparison between Embodiment and Comparative Example 2: Comparing the surface roughness (Rzjis) of the deposit side of the electrolytic copper foil, the electrolytic copper foil of Comparative Example 2 also has a good low profile. However, the surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil incorporated into the present invention is 0.30 μm to 0. The surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil in Comparative Example 2 was 0. The surface roughness (Rzjis) of the precipitation surface of 83 μm and 210 μm electrolytic copper foil incorporated into the present invention is 0.27 μm to 0. Compared to 34 μm , the surface roughness (Rzjis) of the precipitation surface of the 210 μm electrolytic copper foil in Comparative Example 2 was 1. It is 22 μm . Therefore, in Comparative Example 2, it is considered difficult to obtain a stable and smooth electrolytic copper foil because the smoothness of the precipitation surface is impaired by increasing the copper foil thickness. And with regard to mechanical properties, the 12 μm electrolytic copper foil of Comparative Example 2 is normally 31.4 kgf/mm², elongation rate 3.5%, tensile strength after heating 26.8 kgf/mm², 5.8%, and each electrolytic copper foil of the example is superior.

[0122]

Embodiment vs. Comparative Example 3: Comparative Example 3 is for looking at the effect of the absence of MPS or SPS in the copper electrolyte. As is clear from Table 3, the surface roughness (Rzjis) of the precipitation surface of the electrolytic copper foil obtained in Comparative Example 3 without MPS, etc. in the copper electrolyte solution is 3. It shows 60 μm , and low profile has not been achieved. And since the gloss [Gs (60°)] is almost matte, it is 0.7 and very low. The mechanical properties of 12 μm electrolytic copper foil have a tensile strength of 40.5 kgf/mm², showing a large value, but the growth rate is 3. It is 6% lower and the change due to heating is small. Therefore, it can be said that the electrolytic copper foil incorporated into the present invention is superior in terms of surface roughness and elongation rate.

[0123]

Comparison with Embodiment and Comparative Example 4: Comparative Example 4 sees the effect of adding a small molecule plaster instead of MPS to the copper electrolyte. As a result, as can be clearly seen from Table 3, even if a small molecule plaster is included in the copper electrolyte instead of MPS, the surface roughness (Rzjis) of the precipitation surface of the electrolytic copper foil is 3.59 μm is shown, and low profile has not been achieved. And since the degree of gloss [Gs (60°)] is almost matte, 1. It shows a very low value of 0. In terms of mechanical properties, the tensile strength of the normal state is 38.6 kgf/mm² and the same value as the example, but the elongation rate is 4.0%, and as in Comparative Example 3, the change due to heating is small. Therefore, it can be said that the electrolytic copper foil incorporated into the present invention is superior in terms of surface roughness and elongation rate.

[0124]

Embodiment vs. Comparative Example 5: Example vs. Comparative Example 5 is compared between 12 μm electrolytic copper foil products with reference to the data described in Table 5 and Table 6 hereinafter.

[0125]

Comparing the surface roughness (Rzjis) on the precipitation surface side, the electrolytic copper foil obtained in the example is 0.30 μm to 0. It was 41 μm , and the surface roughness (Rzjis) of the precipitation surface was 1. The difference between 00 μm and that is clear. The glossiness of the precipitation surface alone [Gs (60°)] is in the range of 324 to 383 for the electrolytic copper foil obtained in Comparative Example 5, whereas the electrolytic copper foil obtained in the Embodiments is in the completely different range of 603 to 759. That is, compared to the electrolytic copper foil of Comparative Example 5, the electrolytic copper foil of the example has a flatter and closer to the mirror surface. As for the mechanical properties in the normal state, the electrodeposited copper foil of Comparative Example 5 had a tensile strength of 37.9 kgf/mm² and an elongation of 8.0%, while the electrodeposited copper foil of Example 10 had a tensile strength of 35.5 kgf/mm² and an elongation of 11.5%, which showed that the foil was somewhat more flexible. 180°C x 60 min. With regard to the mechanical properties after heating, the electrodeposited copper foil of Comparative Example 5 had a tensile strength of 31.6 kgf/mm² and an elongation of 7.5%, while the electrodeposited copper foil of Example 10 had a tensile strength of 33.2 kgf/mm² and an elongation of 11.2%, showing that the electrodeposited copper foil

of the present invention is superior. Based on these results, considering the heat history when processed into a copper-clad laminate plate, it is possible to expect excellent flex resistance, etc., when using a flexible printed wiring plate using, for example, electrolytic copper foil incorporated into the present invention.

[0126]

Next, we confirmed the superiority of using three types of gloss as an indicator of surface uniformity. When looking at the difference in glossiness with MD as the common direction at the precipitation plane of the 12 μm electrolytic foil obtained in the examples, [Gs (20°)] is 824 to 1206, [Gs (60°)] is 649 to 759, and [Gs (85°)] is 112 to 142, which is larger as the angle of incidence of the measured light approaches vertically. In contrast, looking at the evaluation results obtained in Comparative Example 5, when measured in the MD direction on the precipitation surface side of 12 μm electrolytic copper foil, [Gs (20°)] is 126, [Gs (60°)] is 383, and [Gs (85°)] is 117, and [Gs (20°)] and [Gs (85°)] are almost equivalent. Therefore, the precipitation surface of the 12 μm electrolytic copper foil obtained in Comparative Example 5 has some characteristic shape.

[0127]

Therefore, the SEM photograph of the 12 μm electrolytic copper foil precipitation surface obtained in Embodiment 11 is shown in Figure 1, and the SEM photograph of the 12 μm electrolytic copper foil precipitation surface obtained in Comparative Example 5 is shown in Figure 2. As is clear from Figure 2, in addition to small unevenness being observed on the electrolytic copper foil surface obtained in Comparative Example 5, abnormal precipitation areas that cannot be detected without observation at high magnification are also occasionally observed. That is, the diffuse reflection of light in this uneven part reduces the value of the gloss [Gs (20°)] and increases the surface roughness (Rzjis). In addition, no obvious unevenness was observed in Figure 1, which is an SEM photograph of electrolytic copper foil incorporated into the present invention, and no abnormal precipitation area was observed. Therefore, the electrolytic copper foil according to the present invention has excellent uniform surface roughness and gloss.

[0128]

And when comparing the roughening treated surface treated electrolytic copper foil, in contrast to Embodiment 10 and Comparative Example 5, the increase in the value of surface roughness (Rzjis) due to the roughening treatment performed under the same conditions was approximately 0.7 μm , which is almost the same. As can be seen from Figure 2, the irregularities seen in the precipitation surface shape of the electrolytic copper foil obtained in Comparative Example 5 have a pitch of around 3 μm , but are flat, so it can be inferred that the fine particles obtained from the roughening process adhere along the respective irregularities. However, in the electrolytic copper foil of Comparative Example 5, the surface roughness (Rzjis) of the adhesive surface with the insulating layer component material that is the requirement of the present invention is large because of the surface roughness (Rzjis) of the precipitation surface that is the base. It cannot be less than 5 μm , and the superiority of the electrolytic copper foil pertaining to the present invention is clear.

[0129]

Comparison between MPS and SPS: Examples 9 to 14 use SPS as an alternative to MPS, but the resulting 12 μm electrolytic copper foil has a surface roughness (Rzjis) of 0.30 μm to 0. The 41 μm gloss [Gs (60°)] ranged from 603 to 759, confirming that SPS can have the same effect as MPS.

[0130]

In the above example, when making the electrolytic copper foil incorporated into the present invention, favorable results are obtained with the solution configuration with the copper concentration of the sulfate-based copper electrolyte at 40 g/l to 120 g/l and the free sulfuric acid concentration at 60 g/l to 220 g/l, but it is acceptable to change the concentration range according to the intended application. In addition, the presence of additives other than the additives described in the above examples is not denied, and if it has been confirmed that the effects of the above additives can be further enhanced or contributed to the quality stabilization during continuous production, it is acceptable to add them voluntarily.

[Industrial Availability]

[0131]

The precipitation surface of the electrolytic copper foil incorporated into the present invention has a lower profile than that of the low profile electrolytic copper foil that has been supplied to the conventional market, and the roughness of the precipitation surface is less than or equal to the roughness of the gloss surface, making both sides a glossy smooth surface. And the copper electrolytes that are used in the manufacture of electrolytic foil are subject to fluctuations in the manufacturing conditions.

It is highly adaptable to thickness variations and has excellent productivity. Thus, it is suitable for forming fine pitch circuits of tape automatic bonding (TAB) substrates and chip-on-film (COF) substrates, as well as electromagnetic wave shielding circuits of plasma display panels. In addition, this electrolytic copper foil has excellent mechanical properties, making it suitable for use as a current collector that constitutes a negative electrode, such as a lithium ion secondary battery.

[Brief description of the drawings]

[0132]

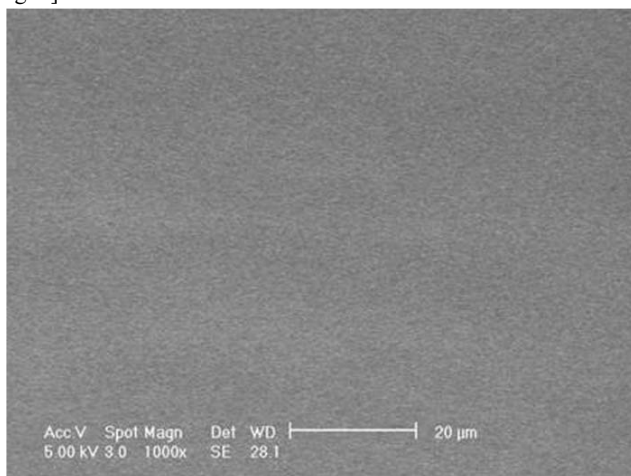
[Fig. 1] SEM photograph of the 12 μm electrolytic copper foil precipitation surface obtained in Example 11.

[Fig. 2] This is an SEM photograph of the 12 μm electrolytic copper foil precipitation surface obtained in Comparative Example 5.

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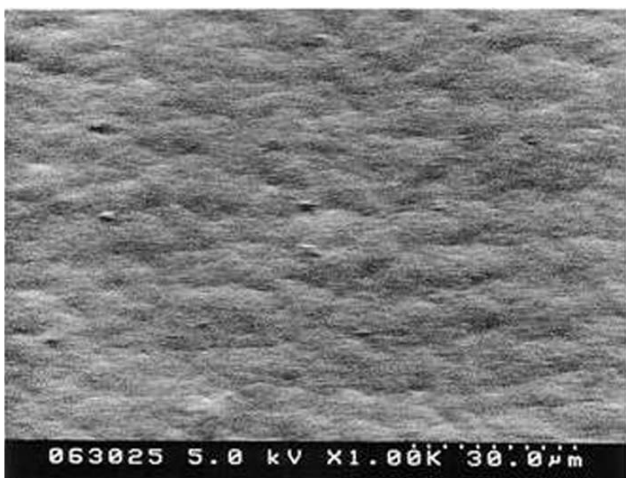
20

[Fig. 1]



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[Fig. 2]



[Procedure Amendment]

[Submission date] December 15, 2006 (2006.12.15)

[Procedural correction 1]

[Name of document subject to correction] Scope of patent claims

[Items subject to correction] Main body

[Correction method] Amendment

[Details of correction]

[Scope of patent claims]

[Claim 1]

Method of stripping copper precipitated on a cathode surface by an electrolytic method using a sulfate-based copper electrolyte to produce an electrolytic copper foil, the method comprising:

A method for producing an electrolytic copper foil characterized in that the sulfate-based copper electrolyte comprises a diallyldimethylammonium chloride polymer and chlorine, which are quaternary ammonium salt polymers having at least one and a cyclic structure selected from 3-mercapto-1-propanesulfonic acid or bis(3-sulfopropyl)disulfide.

[Claim 2]

A total concentration of 3-mercapto-1-propanesulfonic acid and/or bis(3-sulfopropyl)disulfide in the sulfate-based copper electrolyte is 0. The method for producing electrolytic copper foil according to claim 1, characterized in that it is 5 ppm to 100 ppm.

[Claim 3]

Method for making electrolytic copper foil according to Claim 1 or Claim 2, characterized in that the concentration of quaternary ammonium salt polymer having a cyclic structure in the sulfate-based copper electrolyte is 1 ppm to 150 ppm.

[Claim 4]

Method for producing electrolytic copper foil according to any of Claims 1 to 3, characterized in that the chlorine concentration in the sulfate-based copper electrolyte is between 5 ppm and 120 ppm.

[Claim 5]

Electrolytic copper foil characterized in that it was manufactured by the manufacturing method according to any of Claims 1 to 4.

[Claim 6]

The surface treated electrolytic copper foil according to claim 5, wherein one or more of the following types of rust prevention treatment or silane coupling agent treatment were performed on the surface of the electrolytic copper foil.

[Claim 7]

The method of claim 1, wherein the surface roughness (Rzjis) of the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil is 1. The surface treated electrolytic copper foil of Claim 6, characterized in that it is 5 μ m or less.

[Claim 8]

The surface treated electrolytic copper foil of Claim 6 or Claim 7, characterized in that the gloss [Gs (60°)] of the adhesive

surface with the insulating layer construction material of the surface treated electrolytic copper foil is 250 or more.

[Claim 9]

The surface-treated electrolytic copper foil of claim 6, characterized in that the surface-treated electrolytic copper foil has been roughened on the adhesive surface side with the insulating layer construction material.

[Claim 10]

The surface-treated electrolytic copper foil according to any of Claims 6 to 9, characterized in that the adhesive surface of the surface-treated electrolytic copper foil with the insulating layer construction material is on the precipitation surface side of the electrolytic copper foil.

[Claim 11]

A copper-coated laminate plate in which the surface treated electrolytic copper foil of any of Claims 6 to 9 is clung to the insulating layer component material.

[Claim 12]

The rigid copper-clad laminate of claim 11, wherein the insulating layer construction material contains skeletal material.

[Claim 13]

Rigid printed wiring board characterized in that it was obtained using a rigid copper cladding laminate according to claim 12.

[Claim 14]

The flexible copper-clad laminate according to claim 11, wherein the insulating layer construction material is composed of flexible material.

[Claim 15]

A flexible printed wiring board characterized in that it was obtained using the flexible copper-clad laminate according to Claim 14.

[Procedural correction 2]

[Name of document subject to correction] Specifications

[Items subject to correction] Main body

[Correction method] Amendment

[Details of correction]

[Detailed Description of the Invention]

[Technical field]

[0001]

The present invention relates to a method for producing electrolytic copper foil, an electrolytic copper foil obtained by the method for producing it, a surface-treated electrolytic copper foil obtained using the electrolytic copper foil, a copper-coated laminate plate using the surface-treated electrolytic copper foil, and a printed wiring plate. In particular, it relates to an electrolytic copper foil having a low profile and high gloss on the mating surface with the insulating layer construction material of the electrolytic copper foil.

[Background Technology]

[0002]

Because metallic copper is a favorable conductor of electricity, relatively inexpensive and easy to handle, electrolytic copper foil is widely used as the foundation material for printed wiring boards. In addition, for electronic and electrical equipment, where printed wiring boards are often used, it is necessary to reduce the size and weight, etc., so-called light, thin, and small. Conventional

In order to achieve such light, thin, and small electronic and electrical equipment, it is necessary to make the signal circuits as finely pitched as possible, and manufacturers, etc. have responded by adopting thinner copper foil to reduce the time set for over-etching when forming the wiring by etching, and by improving the etch factor of the forming wiring.

[0003]

In addition, demands for enhanced functionality are also being made for electronic and electrical equipment that is miniaturized and lightened. Therefore, in order to ensure the largest possible part mounting area within the limited substrate area due to the spread of surface mounting methods, it has been necessary to take measures to improve the etch factor of the wiring of the printed wiring board. For that purpose, tape automatic bonding (TAB) substrate, which is a so-called interposer substrate that is mounted directly on IC chips, etc., in particular, chi

Low-profile electrolytic copper foil products have been required for up-on-film (COF) substrates beyond normal printed wiring board applications. The profile is defined by the value measured in the TD direction in accordance with JIS B 0 601-2001 for the surface roughness R_{zjs} , which is the bonding interface with the insulating layer-forming material in the standards for copper foil for printed wiring boards (the application uses the term “bonding interface” instead of “bonding surface”). The low profile means that the surface roughness R_{zjs} of the bonding surface is small.

[0004]

In order to solve such problems, Patent Reference 1 discloses a surface treated electrolytic copper foil characterized in that the surface roughness R_z of the precipitation surface of the untreated electrolytic copper foil is the same as or smaller than the surface roughness R_z of the gloss surface of the untreated electrolytic copper foil, and roughening is applied to the precipitation surface of the foil to make the adhesive surface. In addition, the above-mentioned untreated electrolytic copper foil is manufactured using an electrolytic solution with a compound having a mercapto group, a chloride ion, a low molecular weight gutter with a molecular weight of 10,000 or less, and a polymeric polysaccharide. Specifically, the compounds having the mercapto group are 3-mercapto 1-propanesulfonate, the molecular weight of the low molecular weight gut is 3000 or less, and the polymeric polysaccharide is hydroxyethyl cellulose.

[0005]

In addition, Patent Reference 2 discloses a method for producing electrolytic copper foil that is characterized by the use of an electrolytic copper plating solution containing a copolymer of diallyl dialkylammonium salt and sulfur dioxide in a method for producing electrolytic copper foil by electrolysis of an acidic copper plating solution of sulfate. The acid sulfate copper plating solution concerned should contain polyethylene glycol, chlorine and 3-mercapto-1-sulfonic acid. The roughness of the precipitation surface used as the adhesive surface with the insulating substrate is small, and the average roughness R_z of 10 points is $1.0 \mu m \pm 0$. It is said that a low profile of about $5 \mu m$ can be obtained.

[0006]

And when these manufacturing methods are used to produce electrolytic copper foil, a low profile precipitation surface is certainly formed, and it has favorable characteristics as a conventional low profile electrolytic copper foil.

[0007]

[Patent Reference 1] JP 9-143785 Publication

[Patent Reference 2] JP 2004-35918 Publication

[Disclosure of the invention]

[Problem to be solved by the invention]

[0008]

On the other hand, the clock frequency of personal computers, which are representative of electronic or electrical equipment, is increasing, and the computing speed is exponentially faster. In the past, not only data processing, which is the original role of a computer, but also functions that use the computer itself in the same way as an AV device have been added. In other words, not only the music playback function, but also the DVD recording playback function, T V image reception recording function, and video telephone function are added one after another.

[0009]

In other words, it is not enough to simply satisfy the data monitoring function of a personal computer monitor, and image quality is required to withstand long-term viewing even when viewing images such as movies, etc. And it is necessary to supply such quality monitors inexpensively and in large quantities. The current monitor uses a large number of liquid crystal monitors, and it is common to use the aforementioned tape automatic bonding (TAB) substrate and chip-on-film (COF) substrate to mount the driver element of this liquid crystal panel. In addition, in order to achieve high definition of the monitor, the driver board also needs to form a finer circuit to meet the increase in the number of scan lines. In addition, efforts are being made to reduce product dimensions by making the outer edge as narrow as possible as the panel size increases. In order to place the driver on the back, it was necessary to install the TAB substrate or COF substrate by folding, and from the beginning, it was also required to have favorable flexibility. In the COF, unlike TAB, the bonded lead portion is lined with film. Therefore, it is disadvantageous in terms of flexibility compared to TAB without film, and it has better flexibility than before

The use of materials is effective in preventing disconnection.

[0010]

On the other hand, with the spread of hybridization and the development of fuel cell cars in electronic circuits for automotive use, large electric currents are being compelled. Despite the speculation that the conductor thickness required for automotive applications will exceed 200 μm in the future, it is used as a flexible wiring board from the perspective of space saving. In order to apply such thick copper foil to a flexible substrate, it is essential that the adhesive surface roughness of the copper foil is small, and rolled copper foil is also being considered as being unable to be handled with conventional electrolytic copper foil. That is, in the case of conventional electrolytic copper foil, the thicker the thickness, the larger the adhesive surface roughness with the substrate.

[0011]

It is also preferable to use a copper foil with a smooth surface when used as a negative electrode current collector for a lithium ion battery. In other words, when applying active materials on copper foil, it is advantageous to use a copper foil with a smooth surface as a current collector in order to coat a slurry containing active materials on copper foil with uniform coating thickness. In addition, because the negative electrode active material in question repeatedly expands and deflates during charging and discharging, there is also a large change in the size of copper foil as a current collector material, and the expansion and deflation cannot follow the expansion and deflation behavior of copper foil, resulting in a phenomenon of breaking. Thus, the mechanical properties of the copper foil, which is a current collector, withstand repeated expansion and contraction behavior, so a favorable balance of tensile strength and elongation is required. Furthermore, it is equally advantageous to use a smooth surface copper foil when forming a dielectric layer for capacitors on copper foil by sol-gel method.

[0012]

As described above, the market has been expanding for electrolytic copper foil due to the use of printed wiring boards. As a result, it became clear that there was a demand for electrolytic copper foil with a lower profile at a thickness of 450 μm or less and favorable flexibility compared to the low profile electrolytic copper foil for printed wiring board applications that have been supplied to the conventional market.

[Means for Solving the Problems]

[0013]

Based on the above background, the present inventors conceived of a method for producing low-profile electrolytic copper foil that has productivity that is not inferior to conventional electrolytic copper foil production technology as a result of keen research.

[0014]

Methods of producing electrolytic copper foil incorporated into the present invention: The method for producing the electrolytic copper foil incorporated into the present invention is characterized by a method of stripping copper precipitated on the cathode surface by electrolytic method using a sulfate-based copper electrolyte, wherein the sulfate-based copper electrolyte comprises a polymer and chlorine, which are quaternary ammonium salt polymers having at least one type and cyclic structure selected from 3-mercapto-1-propanesulfonic acid (hereinafter referred to as [MPS] in the present application) or bis(3-sulfopropyl) disulfide (hereinafter referred to as [SPS] in the present application).

[0015]

In the manufacturing method of the electrolytic copper foil incorporated into the present invention, the combined concentration of MPS and/or SPS in the sulfate-based copper electrolyte is 0. It is preferable to use between 5 ppm and 100 ppm.

[0016]

In the manufacturing method of the electrolytic copper foil incorporated into the present invention, it is desirable that the concentration of quaternary ammonium salt polymer having a cyclic structure in the sulfate-based copper electrolyte is 1 ppm to 150 ppm.

[0017]

Furthermore, in the manufacturing method of the electrolytic copper foil incorporated into the present invention, the chlorine concentration in the sulfate-based copper electrolyte is preferably between 5 ppm and 120 ppm.

[0018]

Electrolytic copper foil according to the present invention: The electrolytic copper foil incorporated into the present invention is an electrolytic copper foil characterized in that it was manufactured by the above-mentioned method for producing electrolytic copper foil.

[0019]

Surface treated electrolytic copper foil incorporated into the present invention: The surface-treated electrolytic copper foil incorporated into the present invention is described in the above-described electrolytic

One or more of rust-prevention or silane coupling agent treatment has been performed on the surface of copper foil.

[0020]

In addition, the surface roughness (R zjis) of the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil incorporated into the present invention is 1. It is preferably 5 μm or less.

[0021]

In addition, it is preferable to use a surface treated electrolytic copper foil with a gloss [Gs (60°)] of 250 or more as the adhesive surface with the insulating layer construction material according to the present invention.

[0022]

In addition, it is preferred that the surface treated electrolytic copper foil incorporated into the present invention be roughened on the adhesive surface side of the surface treated electrolytic copper foil with the insulating layer component material.

[0023]

In addition, it is preferable to use the precipitation surface of the above-mentioned electrolytic copper foil as the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil incorporated into the present invention.

[0024]

Copper-coated laminates according to the present invention: The copper-clad laminate according to the present invention is obtained by clinging the surface treated electrolytic copper foil and insulating layer construction material. In addition, in the case where the insulating layer component material comprising the copper-clad laminate according to the present invention contains skeletal material, it is a rigid copper-clad laminate. On the other hand, in the case where the insulating layer construction material comprising the copper-clad laminate according to the present invention is a flexible material having flexibility, it is a flexible copper-clad laminate.

[0025]

Printed Wiring Boards for the Invention: A copper-clad laminate can be obtained using the surface treated electrolytic copper foil incorporated into the present invention, and by etching this copper-clad laminate, a printed wiring plate according to the present invention can be obtained. That is, a rigid printed wiring board can be obtained by using the rigid copper cladding laminate described above. In addition, flexible printed wiring boards can be obtained by using the flexible copper-clad laminate mentioned above.

[Effect of the Invention]

[0026]

The method for producing the electrolytic copper foil incorporated into the present invention includes DDAC polymer and chlorine, which are quaternary ammonium salt polymers having a cyclic structure with at least one type selected from MPS or SPS, as the electrolytic solution for the sulfate-based copper electrolyte. And the electrolytic copper foil obtained in this manufacturing method

, it has even better low profile properties than the low profile electrolytic copper foil that has been supplied to the conventional market. As a result, the lower the profile of the method for producing the electrolytic copper foil incorporated into the present invention becomes more pronounced as the thickness increases as the electrolytic copper foil to be manufactured. This trend is the opposite of conventional electrolytic copper foil products, which profile higher with increasing thickness.

[0027]

In addition, when this electrolytic copper foil is actually supplied to the market, various surface treatments are applied to prevent oxidation due to atmosphere and improve adhesion to the substrate, and are generally supplied as surface treated electrolytic copper foil. By using the electrolytic copper foil incorporated into the present invention, it is possible to achieve a low profile that exceeds the low profile electrolytic copper foil applied to the market even if the surface treatment is performed as long as such surface treatment is performed properly.

[0028]

Therefore, when the surface-treated electrolytic copper foil incorporated into the present invention is used in a copper-coated laminated plate, the thickness uniformity of the insulating layer located between the conductor layers composed of the surface-treated electrolytic copper foil incorporated into the present invention is excellent, and even when a thin insulating layer is used, the insulation reliability between the layers is dramatically improved without causing a short circuit. In particular, a uniform roughening process makes it suitable for high frequency copper coated laminates.

[0029]

Furthermore, the printed wiring board obtained by etching the copper coated laminate according to the present invention is suitable for the formation of fine pitch circuits because it is possible to reduce the profile of the surface treated electrolytic copper foil incorporated into the present invention used in the copper coated laminate.

[Best Embodiments of the Invention]

[0030]

[Form of the method for producing electrolytic copper foil incorporated into the present invention]

Before explaining the method for producing electrolytic copper foil incorporated into the present invention, we will state the general method for producing electrolytic copper foil so that it is easier to understand the explanation. [Electrolytic copper foil] pertaining to the present invention is a condition in which no surface treatment has been performed, and it may be referred to as [untreated copper foil], [segregation and separation foil], etc. In the present specification, this is simply referred to as [electrolytic copper foil]. The production of this electrolytic copper foil generally employs a continuous production method,

in which a sulfate-based copper electrolyte is flowed between a rotating cathode in a drum shape and a lead-based anode or a dimensionally stable anode (DSA) disposed oppositely along the shape of the rotating cathode, and the copper is precipitated onto the surface of the rotating cathode using an electrolytic reaction, and this precipitated copper is continuously peeled away from the rotating cathode as a foil state and wound. Since the electrolytic copper foil obtained in this way is a roll wound at a constant width, the rotational direction of the rotating cathode (length direction of the web) is referred to as the MD (Machine Direction) and the transverse direction of the width direction perpendicular to the MD is referred to as the TD (Transverse Direction).

[0031]

The surface shape of the side peeled off from the state in contact with the rotating cathode of this electrolytic copper foil has been referred to as the “gloss surface” because the shape of the polished rotating cathode surface has a gloss. On the other hand, the surface shape on the side that was the precipitation side shows the uneven shape of the peak shape because the crystal growth rate of copper that normally precipitates varies from crystal surface to surface, and this side is referred to as the “precipitation surface.” In general, the roughness of the precipitation surface is greater than the roughness of the glossy surface, and when surface treatment is applied to the electrolytic copper foil, the roughening treatment is often applied to the precipitation surface side, and this precipitation surface side becomes the mating surface with the insulating layer component material when producing the copper-clad laminate. Thus, the smaller the surface roughness of this adhesive surface, the better the low profile surface treated electrolytic copper foil.

[0032]

In this way, the electrolytic copper foil is subjected to a surface treatment such as roughening treatment and oxidation prevention to reinforce the adhesion of the insulating layer component material with a mechanical anchoring effect, and the electrolytic copper foil that distributes the market is completed, but it may be used without roughening treatment depending on the application. Next, the manufacturing method of the electrolytic copper foil incorporated into the present invention is described below.

[0033]

The method for producing the electrolytic copper foil incorporated into the present invention is characterized by a method of stripping copper deposited on the cathode surface by electrolytic method using a sulfate-based copper electrolyte, wherein the sulfate-based copper electrolyte comprises a DDAC polymer, a quaternary ammonium salt polymer having a cyclic structure with at least one type selected from MP S or SPS, and chlorine. By using this composition of sulfate-based copper electrolyte, it is possible to manufacture electrolytic copper foil with a low profile according to the present invention stably. Furthermore, by optimizing the electrolytic conditions, the electrolytic copper foil with a gloss [Gs (60°)] of greater than 700 can be obtained. The concentration of copper in this sulfate-based copper electrolyte is 40 g/l to 120 g/l, and the more preferred range is 50 g/l to 80 g/l. In addition, the concentration of free sulfuric acid in the sulfate-based copper electrolyte is 60 g/l to 220 g/l, and the more preferred range is 80 g/l to 150 g/l.

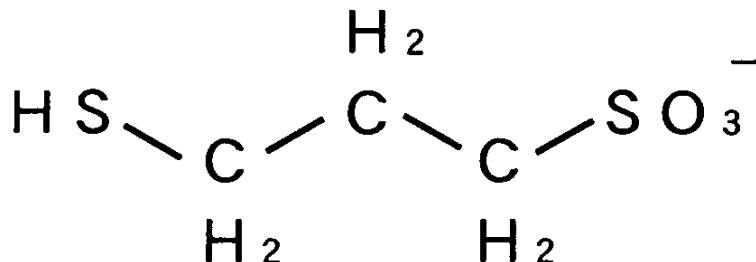
[0034]

The combined concentration of MPS and/or SPS in the sulfate-based copper electrolyte according to the present invention is 0.5 ppm to 100 ppm is preferred, more preferably 0.5 ppm to 50 ppm, more preferably 1 ppm to 30 ppm. The concentration of this MPS and/or SPS is 0. When less than 5 ppm, the precipitation surface of the electrolytic copper foil becomes rough, making it difficult to obtain a low profile electrolytic copper foil. On the other hand, even if the concentration of MPS and/or SPS exceeds 100 ppm, the effect of smoothing the precipitation surface of the resulting electrolytic copper foil does not improve, and only increases the cost of waste treatment. Furthermore, MPS and/or SPS as described in the present invention are used in the sense that each salt is also included, and the stated value of concentration is the equivalent value of sodium 3-mercaptopropylsulfonate as a sodium salt (hereinafter referred to as “MPS-Na” in the present application).

In addition, MPS adopts the SPS structure by dimerizing in the sulfate-based copper electrolyte according to the present invention. Therefore, the concentration of MPS or SPS is a concentration that includes salts such as 3-mercapto-1-propanesulfonic acid alone and MPS-Na, as well as those added as SPS and denatures polymerized into SPS, etc. after being added to the electrolyte as MPS. The following shows the structural formula of MPS as Clarification 1 and the structural formula of SPS as Clarification 2. The comparison of these structural formulas shows that the SPS structure is a binary of the MPS.

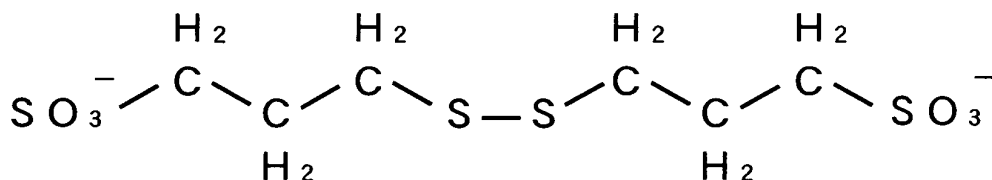
[0035]

[Reaction 1]



[0036]

[Reaction 2]

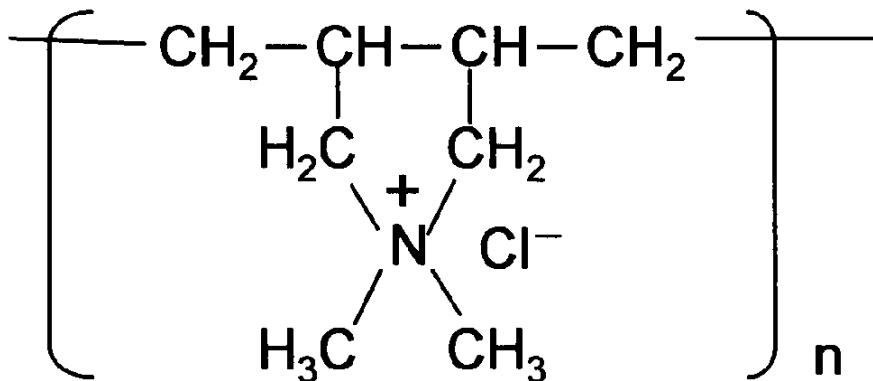


[0037]

In addition, the quaternary ammonium salt polymer having a cyclic structure in the sulfate-based copper electrolyte according to the present invention preferably has a concentration between 1 ppm and 150 ppm, more preferably between 10 ppm and 120 ppm, and even more preferably between 15 ppm and 40 ppm. Here, it is possible to use a variety of quaternary ammonium salt polymers having a cyclic structure. However, given the effect of forming a low profile precipitation surface, it is most preferred to use a DDAC polymer. DDACs form a cyclic structure when taking the polymer structure, and some of the cyclic structure will consist of nitrogen atoms of quaternary ammonium. The DDAC polymers are considered to be any of the 4-membered rings to 7-membered rings or mixtures thereof, and the compounds taking the 5-membered ring structure of these polymers are shown below as representative 3. This DDAC polymer is a polymer structure in which the DDAC has more than two monomers, as can be clearly understood from Reaction 3.

[0038]

[Reaction 3]



[0039]

The concentration in the sulfate-based copper electrolyte of this DDAC polymer is preferably between 1 ppm and 150 ppm, more preferably between 10 ppm and 120 ppm, and even more preferably between 15 ppm and 40 ppm. When the concentration of DDAC polymer in the sulfuric acid copper electrolyte is less than 1 ppm, no matter how much the concentration of MPS or SPS is increased, the deposited copper surface becomes rough, making it difficult to obtain low-profile electrolytic copper foil. On the other hand, if the concentration in the sulfate-based copper electrolyte of the DDAC polymer exceeds 150 ppm, the precipitation state of copper becomes unstable, making it difficult to obtain low-profile electrolytic copper foil.

[0040]

Further, the chlorine concentration in the sulfate-based copper electrolyte is preferably between 5 ppm and 120 ppm, and more preferably between 10 ppm and 60 ppm. If this chlorine concentration is less than 5 ppm, the precipitation surface of the electrolytic copper foil becomes coarse and it is not possible to maintain a low profile. On the other hand, even if the chlorine concentration exceeds 120 ppm, the precipitation surface of the electrolytic copper foil becomes coarse, and the electrostatic condition is not stable, and the precipitation surface with a low profile cannot be formed.

[0041]

As described above, the component balance between MPS and/or SPS and DDAC polymer and chlorine in the sulfate-based copper electrolyte is most important, and if these quantitative balances deviate from the above range, the precipitation surface of the electrolytic copper foil will become coarse as a result, and it will not be possible to maintain a low profile.

[0042]

In addition, in the case where the aforementioned sulfate-based copper electrolyte is used to produce electrolytic copper foil, electrolytic is performed using a cathode and an insoluble anode with a surface roughness adjusted to a predetermined range. At this time, the liquid temperature is preferably 20°C to 60°C, more preferably 40°C to 55°C, the current density is preferably 15A/dm² to 90A/dm², more preferably 50A/dm² to 70A/dm².

[0043]

In addition, in the case of the method of manufacturing the electrolytic copper foil incorporated into the present invention, in order to obtain the properties required for the electrolytic copper foil described above stably, the cathode surface condition should also be managed when manufacturing the same. Referring to JIS C 6515, which is the standard for electrolytic copper foil for printed wiring boards, the surface roughness (Rzjis) of the glossy surface required for electrolytic copper foil is at most 2. It is specified to be 4 μm. When a rotating cathode drum of titanium (Ti) material is used as the cathode for the production of this electrolytic copper foil, the appearance and metal phase changes due to surface oxidation occur during continuous use. Therefore, a mechanical machining operation of regular surface polish, conditional polishing or cutting is required. Such mechanical processing of the cathode surface is performed while rotating the cathode, so a circumferentially muscular processing pattern inevitably occurs. For this reason, the aforementioned standard values are allowed, assuming that it is difficult to maintain the surface roughness (Rzjis) of the glossy surface at steady state while remaining small, and that there is no hindrance to the manufacturing of printed wiring boards from a cost perspective.

[0044]

In the case of conventional electrolytic copper foil, the thicker the thickness, the greater the precipitation surface roughness. And as another factor, the use of a cathode drum with a surface roughness at or above the upper limit of the standard value tends to increase the roughness of the precipitation surface of the resulting electrolytic copper foil due to the influence of the surface shape of the cathode. On the other hand, when using the copper sulfate-based electrolyte described above, the film thickness is less susceptible to the cathode surface shape as it grows while filling the irregularities of the cathode surface, and it is possible to form a flat precipitation surface. In other words, compared to the copper electrolyte used in the manufacture of conventional electrolytic copper foil, when the above-mentioned copper sulfate-based electrolyte is used to manufacture electrolytic copper foil, it is less susceptible to the shape of the cathode surface, and it is possible to use a cathode with a rough surface.

[0045]

For example, in the case of the manufacture of electrolytic copper foil having a thickness of less than 20 μm , the precipitation surface roughness (Rzjis) of the resulting electrolytic copper foil is 1. If less than 0 μm , the surface roughness (Rzjis) of the glossy surface of the electrolytic copper foil is 2. Using a cathode in a surface state such that the gloss [Gs (60°)] is 70 or greater at less than 0 μm is preferred in terms of reducing the difference between mechanical and surface properties in the TD direction and the MD direction. And more preferably, the surface roughness (Rzjis) of the glossy surface of the electrolytic copper foil is 1. It is preferable from a similar perspective to use a cathode in a surface state such that the gloss [Gs (60°)] is 100 or greater at less than 7 μm .

[0046]

[Form of electrolytic copper foil incorporated into the present invention]

The electrolytic copper foil incorporated into the present invention is characterized in that it was manufactured by the above-mentioned method for producing electrolytic copper foil. The properties of the electrolytic copper foil obtained by this manufacturing method are described below.

[0047]

The electrolytic copper foil incorporated into the present invention has a surface roughness (Rzjis) of 1. Less than 0 μm and with a gloss [Gs (60°)] of 400 or more. More preferably, surface roughness (Rzjis) is 0. Less than 6 μm , gloss [Gs (60°)] is greater than 600. First, we will explain the gloss. Here, the gloss of [Gs (60°)] is a measurement of the intensity of light irradiated to the surface of the electrolytic copper foil at an incident angle of 60° and bounced back at a reflection angle of 60°. The angle of incidence referred to here is 0°, which is the perpendicular direction to the surface irradiated with light. In addition, according to JIS Z 8741-1997, five mirror gloss measurement methods with different angles of incidence are described, and it is said that the optimal angle of incidence should be selected according to the gloss of the sample. Among other things, it is said that by setting the angle of incidence to 60°, it is possible to measure a wide range of samples from low gloss to high gloss. Therefore, 60° was mainly used for the gloss measurement of electrolytic copper foil, etc., according to the present invention.

[0048]

In general, surface roughness Rzjis has been used as a parameter to evaluate the smoothness of the precipitated surface of electrolytic copper foil. However, Rzjis alone can only obtain uneven information in the height direction, and cannot obtain information such as uneven cycles or undulations. Because gloss is a parameter that reflects the information of both, various parameters such as the roughness cycle of the surface, undulation, and uniformity within those surfaces can be determined together when used in conjunction with Rzjis.

[0049]

In the case of electrolytic copper foil incorporated into the present invention, the surface roughness (Rzjis) on the precipitation surface side is 1. It is less than 0 μm and the gloss [Gs (60°)] of the precipitation surface is 400 or greater. In other words, electrolytic copper foil that can guarantee quality within such a range and that can be supplied to the market did not exist in the past. By using the manufacturing method described below appropriately, the surface roughness (Rzjis) is 0. Less than 6 μm , the gloss [Gs (60°)] can also provide electrolytic copper foil with more than 700 precipitation surfaces. In addition, although there is no upper limit for gloss, it is limited to about 780 at [Gs (60°)] based on empirical judgment. The glossiness of the present invention was measured using a glossometer VG-2000 model manufactured by Nihon Denko Co., Ltd. in accordance with JIS Z 8741-1997, which is a method of measuring glossiness.

[0050]

And with regard to the electrolytic copper foil products mentioned here, there are no limitations on the thickness. This is because, as the thickness

increases, there is a favorable tendency that the roughness of the deposition surface becomes smaller and the glossiness increases. If the upper limit is set, it is targeted at electrolytic copper foil with a thickness of 450 μm or less, which is a limit that can be profitable even when industrially manufacturing electrolytic copper foil.

[0051]

Also, the lower limit of surface roughness (R_{zjs}) on the precipitation surface side is not limited here. The lower limit of surface roughness is empirically 0. It is about 1 μm . However, in the actual measurement, variation is seen, and the lower limit as a guaranteed measurement value is 0. It is considered to be about 2 μm .

[0052]

In addition, the electrolytic copper foil incorporated into the present invention takes the gloss [Gs (60°)] on the side of the precipitation surface divided into the TD gloss measured in the width direction and the MD gloss measured in the flow direction, and when this ratio ([TD gloss] / [MD gloss]) is taken, it is 0.9 - 1. It is in the range of 1. This means that the difference between the width direction and the flow direction is very small.

[0053]

In other words, it was common knowledge that electrolytic copper foil has different mechanical properties between the width direction (TD) and the flow direction (MD) due to the influence of abrasive streaks, etc., on the surface of the rotating drum which is a cathode. However, the electrolytic copper foil incorporated into the present invention has a more uniform and smooth surface on the precipitation surface regardless of thickness, and the gloss [Gs (60°)] as its appearance is a value of [TD gloss] / [MD gloss] of 0.9 - 1.1, and the change width is small at within 10%, meaning that the surface shape variation between the TD direction and the MD direction of the electrolytic copper foil pertaining to the present invention is extremely small.

[0054]

Furthermore, the fact that there is no difference in appearance in the TD direction and MD direction means that uniform electrolysis is performed, and even in the crystal structure, it is uniform. That is, it means that the difference in mechanical properties such as tensile strength and elongation rate will also be reduced depending on the TD direction and MD direction. If the difference in mechanical properties between the TD direction and the MD direction is thus small, the effect of the direction of copper foil on the substrate dimensional change rate and circuit linearity, etc. when manufacturing the printed wiring board is small and preferred. Incidentally, in the case of rolled copper foil, which can be said to be representative of copper foil having a smooth surface, it is widely known that the mechanical properties of the TD direction and the MD direction differ due to the processing method. As a result, the film carrier tape market, which is the application envisioned by the present invention, and thin rigid printed wiring boards, etc., have a large dimensional change rate, and it has been evaluated that they are not suitable for fine pattern applications.

[0055]

By using [Gs (20°)] and [Gs (60°)] as gloss, the difference between conventional low-profile electrolytic copper foil can be more clearly seen. Specifically, the electrolytic copper foil incorporated into the present invention can have a relationship between the aforementioned precipitation surface [Gs (20°)] > [Gs (60°)]. The same material is expected to be sufficient to evaluate the glossiness by selecting one angle of incidence, but since the reflectance varies depending on the angle of incidence, if the angle of incidence changes, the spatial distribution of reflected light changes depending on the irregularities of the surface of the measured surface, resulting in a difference in gloss. Based on these facts, the inventors, etc. in this case examined the results, and found that there was an empirical tendency to: That is, in the case of high-gloss and low-surface roughness electrolytic copper foil, a relationship between gloss [Gs (20°)] > gloss [Gs (60°)] > gloss [Gs (85°)] is established, and in the case of low-gloss and low-surface roughness electrolytic copper foil, a relationship between gloss [Gs (60°)] > gloss [Gs (20°)] > gloss [Gs (85°)] is established. Furthermore, in the case of electrolytic copper foil products of glossless and low surface roughness, the relationship between gloss [Gs (85°)] > gloss [Gs (60°)] > gloss [Gs (20°)] is established. As can be seen above, in addition to the absolute value of gloss at a constant angle of incidence, it is meaningful to evaluate smoothness by relation to gloss measurements at different angles of incidence.

[0056]

In the case of electrolytic copper foil incorporated into the present invention, the surface condition of the gloss surface is also important. This gloss surface includes a surface roughness (R_{zjs}) at a level close to the precipitation surface of the electrolytic copper foil incorporated into the present invention, and

gloss [Gs (60°)] is required. That is, in the electrolytic copper foil incorporated into the present invention, the gloss

surface side has a surface roughness (Rzjis) of 2. Preferably, it is less than $0\ \mu\text{m}$ and has a gloss [Gs (60°)] of 70 or greater. More preferably, the surface roughness (Rzjis) is 1. It is desirable to have a gloss [Gs (60°)] of less than $7\ \mu\text{m}$ and greater than 100. The upper limit of the gloss [Gs (60°)] is not specified, but empirically it is at 500. That is, in order to obtain the surface condition of the precipitation surface described so far, it is preferable to form a surface condition as described herein on the glossy surface. If this condition is removed, it is likely that the surface conditions will differ in the TD direction and MD direction, and it is also likely that mechanical property differences such as tensile strength and elongation rate will occur in the TD direction and MD direction. The surface condition of this shiny surface is a transcription of the surface condition of the cathode, which is the electrodeposition surface, and is determined by the surface condition of the cathode. Therefore, especially when producing thin electrolytic copper foil, the surface roughness (Rzjis) of the cathode surface is 2. Characterization of less than $0\ \mu\text{m}$ is required.

[0057]

The mechanical properties of the electrolytic copper foil incorporated into the present invention are tensile strength of $33\ \text{kgf/mm}^2$ or more and elongation rate of 5% or more in normal conditions. After heating ($180^\circ\text{C} \times 60$ minutes, atmosphere), the tensile strength is preferably $30\ \text{kgf/mm}^2$ or more, and the elongation rate is 8% or more.

[0058]

In addition, in the present invention, by optimizing the manufacturing conditions, it is possible to have superior mechanical properties such as a normal tensile strength of $38\ \text{kgf/mm}^2$ or more, and a tensile strength of $33\ \text{kgf/mm}^2$ or more after heating ($180^\circ\text{C} \times 60$ minutes, atmosphere). Thus, this favorable mechanical property is not only sufficiently resistant to the folding use of flexible printed circuit boards, but is also suitable for current collection material applications that constitute a negative electrode, such as a lithium ion secondary battery that undergoes expansion and contraction behavior.

[0059]

[Form of surface treated electrolytic copper foil incorporated into the present invention]

The surface-treated electrolytic copper foil incorporated into the present invention provides surface-treated electrolytic copper foil that has undergone one or more of rust prevention treatment or silane coupling agent treatment on the surface of the electrolytic copper foil described above. This rust-prevention treatment layer is intended to prevent oxidative corrosion of the surface of the electrolytic copper foil so as not to interfere with the manufacturing process of the copper-clad laminate and printed wiring boards. It is then recommended that the configuration be improved if possible without inhibiting adhesion to the insulating layer component material. The method used for the rust prevention treatment is not problematic even if organic rust prevention using benzotriazole, imidazole, etc., or inorganic rust prevention using zinc, chromate, zinc alloy, etc., or both are used in combination.

[0060]

The silane coupling agent treatment is a treatment to chemically improve adhesion with the insulating layer component material after the rust prevention treatment has ended.

[0061]

Next, methods of forming a rust-prevention treatment layer will be described. In the case of organic rust prevention, it is possible to form the organic rust prevention agent solution by immersion application, shower ring application, electroplating method, etc. In the case of inorganic rust prevention, it is possible to use a method of electrolytically exposing rust prevention elements onto the surface of electrolytic copper foil, other so-called displacement precipitation methods, etc. For example, when zinc rust prevention treatment is performed, zinc pyrophosphate galvanized bath, zinc cyanide galvanized bath, zinc sulfate galvanized bath, etc. can be used. For example, in a galvanized pyrophosphate bath, the concentration is zinc 5 g/l to 30 g/l, potassium pyrophosphate 50 g/l to 500 g/l, liquid temperature 20°C to 50°C , pH 9 to 12, current density 0. The condition is set to 3 A/dm² to 10 A/dm².

[0062]

In addition, the silane coupling agent used in the above-mentioned silane coupling agent treatment is not particularly limited, and it is possible to optionally use epoxy-based silane coupling agent, amino-based silane coupling agent, mercapto-based silane coupling agent, etc., taking into account the properties of the insulating layer construction material used, plating liquid used in the printed wiring plate manufacturing process, etc. In

addition, the silane coupling agent treatment can then be performed by employing a silane coupling agent solution by dip coating, showering coating, electrodeposition, or other methods.

[0063]

More specifically, it is possible to use coupling agents similar to those used in glass cloth of prepregs for printed wiring boards, such as vinyltrimethoxysilane, vinylphenyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, 4-glycidylbutyltrimethoxysilane, γ -aminopropyltriethoxysilane, N- β -(aminoethyl) γ -aminopropyltrimethoxysilane, N-3-(4-(3-aminopropoxy) butoxy) propyl-3-aminopropyltrimethoxysilane, imidazole silane, triazine silane, and γ -mercaptopropyltrimethoxysilane.

[0064]

The surface roughness (Rzjis) of the adhesive surface with the insulating layer construction material of the surface treated electrolytic copper foil is 1. Preferably, it has a low profile of 5 μm or less. Surface roughness is adjusted to this range, making it a surface treated copper foil suitable for forming fine pitch circuits.

[0065]

It is also preferred that the gloss [Gs (60°)] of the adhesive surface of the surface treated electrolytic copper foil with the insulating layer construction material is 250 or greater. Because surface treatment forms a rust-prevention coating or a silane coupling agent coating, even at levels where no changes in surface roughness are detected, it is conceivable that the reflectance of light, etc. will change in comparison before and after surface treatment. Thus, although the absolute gloss value may vary after surface treatment, it can be determined that the surface treatment coating is formed at the appropriate thickness if the gloss [Gs (60°)] obtained at the surface treatment electrolytic copper foil adhesive surface is maintained at 250 or higher.

[0066]

It is also preferred that the surface treated electrolytic copper foil is subjected to a roughening treatment on the adhesive surface with the insulating layer construction material. The roughening treatment can be applied to known technologies, and it is sufficient to perform the minimum necessary roughening treatment based on the combination with the rust prevention technology. However, in the formation of fine pitch wiring such that the surface treated electrolytic copper foil incorporated into the present invention is preferably less than the 25 μm pitch used, it is preferable to increase the accuracy of the over-etching time required.

[0067]

In addition, as a method of roughening, either a fine metal grain is adhered to the surface of the electrolytic copper foil, or a roughening surface is formed by an etching method is employed. Here, as a method of depositing the former fine metal grains, a method of depositing the copper fine grains onto a surface is illustrated. This roughening process consists of precipitating and depositing fine copper particles on the surface of the electrolytic copper foil, and over-plating steps to prevent this fine copper particle from falling out.

[0068]

In the process of precipitating and adhering fine copper particles onto the surface of the electrolytic copper foil, the conditions of stake plating are adopted as the electrolytic conditions. Therefore, in general, the solution concentration used in the process of precipitating and depositing fine copper granules is low so that it is easy to create a smear plating condition. This smudge plating condition is not particularly limited, but is determined in consideration of the characteristics of the production line. For example, if a copper sulfate solution is used, the concentration is 5 to 20 g/l copper, 50 to 200 g/l free sulfate, other additives as necessary (α -naphthokinoline, dextrin, gut, thiourea, etc.), liquid temperature is 15 to 40°C, and current density is 10 to 50 A/dm².

[0069]

In addition, the coating plating process to prevent the dropping of fine copper grains is a process to uniformly precipitate copper so that the fine copper grains are coated according to smooth plating conditions. Thus, a copper electrolyte similar to that used in the aforementioned electrolytic copper foil manufacturing process can be used here as a source of copper ions. This smooth plating condition is not particularly limited, but is determined in consideration of the characteristics of the production line. For example, if a copper sulfate solution is used, the conditions are as follows: copper concentration 50

to 80 g/l, free sulfuric acid 50 to 150 g/l, solution temperature 40 to 50° C., and current density 10 to 50 A/dm².

[0070]

In addition, it is said that the adhesive surface of the surface treated electrolytic copper foil with the insulating layer construction material is preferably on the precipitation surface side. As mentioned above, it is difficult to eliminate any difference in the TD direction/MD direction because the surface shape of the cathodic drum is a transferred shape. Therefore, it is preferable to use the precipitation surface side as the adhesive surface in order to minimize the linearity variation of the wiring end surface that occurs when the shape of the adhesive surface has direction in TD/MD.

[0071]

[Form of copper-clad laminate according to the present invention]

The present invention provides a copper-clad laminate of said surface-treated electrolytic copper foil to be clung to an insulating layer construction material. With regard to the manufacturing method of these copper-clad laminates, it is possible to use the conventional method of roll laminate or casting method for flexible copper-clad laminates, and it is possible to manufacture rigid copper-clad laminates using a hot press or continuous laminate method. It should be noted that the flexible copper-clad laminate and rigid copper-clad laminate described in the present invention are concepts that include all of a single-sided copper-clad laminate, a double-sided copper-clad laminate, and a multi-layer copper-clad laminate. Here, in the case of a multi-layer copper-clad laminate, the surface treated copper foil according to the present invention is used as the outer layer, and the inner layer comprises an inner layer core material comprising an inner layer circuit. In the following description of the copper coated laminate, there is no explanation to distinguish between them. This is because it will be duplicated.

[0072]

The present invention provides a rigid copper cladding laminate in which the insulating layer construction material contains skeletal material. It has been reported that the majority of the skeletal materials used in conventional rigid copper-clad laminates are glass woven or non-woven, and the roughness of the copper foil adhesive surface affects interlayer insulation at levels above $10\text{ }\mu\text{m}$, and migration resistance due to direct contact between the glass fiber, which is the skeletal material, and the circuit even at $10\text{ }\mu\text{m}$ or less can be problematic. At the $5\text{ }\mu\text{m}$ level, it was said that there was no cause for concern. However, in recent years, for example, BGA and CSP, which are package substrates that are directly mounted with electronic components, have also been required to have a fine pattern that has not been conventionally done, and the surface has been flattened by using aramid fibers thinner than glass fibers as skeletal material in nonwoven fabric. Furthermore, when components, etc., with higher clock frequencies are installed, the transmission characteristics of the signal in the high frequency range are not satisfied when the linearity and cross-sectional shape of the circuit are far from the ideal state. Therefore, the copper-clad laminate according to the present invention is suitable for the manufacturing application of printed wiring boards having transmission circuits of high frequency signals, not only fine patterns.

[0073]

In addition, the present invention provides a flexible copper-clad laminate plate composed of flexible materials that are flexible in the insulating layer construction materials described above. Flexible copper-clad laminates have been separated from rigid copper-clad laminates in terms of flexibility and light weight, and insulating layer materials have been made thinner to achieve light weight and high flexibility. At the same time, thinning is also required for the conductor layer, and electrolytic copper foil is the main material. In addition, in order to ensure insulation reliability in thin films, especially in multilayer flexible substrate applications, a low profile of less than 1/10 of the thickness of the insulating layer is required for the adhesive surface, so in the case of conventional products, the above surface roughness $R_{zjis} = 5\text{ }\mu\text{m}$ was the upper limit of use. However, the flexible copper-clad laminate using the electrolytic copper foil of the present invention can ensure insulation reliability even if the film thickness is further reduced. In addition, it has superior flexibility compared to the flexible copper-clad laminate using conventional low-profile electrolytic copper foil, and it is also a copper-clad laminate with improved reliability in this regard.

[0074]

Here, a method for producing rigid copper-clad laminates and flexible copper-clad laminates is specifically illustrated. When producing a rigid copper-clad laminate or a flexible copper-clad laminate, a desired layup state is formed using the surface-treated electrolytic copper foil according to the present invention, a rigid insulating layer-forming material such as an FR-4 class prepreg or a flexible insulating layer-forming material such as a polyimide resin film, and a panel, and then hot press-molded at 170°C to 200°C .

[0075]

On the other hand, in the case of a flexible copper-clad laminate, it is possible to adopt the roll laminate method and casting method as described above. This roll laminate method is a method of thermal crimping at the pressure of a heating roll using a roll of surface treated copper foil according to the present invention and a roll of resin film such as polyimide resin film and PET film. The casting method is to form a resin composition film that becomes polyimide resin by heating polyamic acid, etc., on the surface of the surface treated copper foil according to the present invention, and directly form a polyimide resin film on the surface of the surface treated copper foil by heating to cause a condensation reaction.

[0076]

[Form of printed wiring board according to the present invention]

In addition, the present invention provides a rigid printed wiring board characterized in that it was obtained using the aforementioned rigid copper-clad laminate. As described above, in the manufacture of printed wiring boards using the copper-clad laminate using the electrolytic copper foil with a smooth adhesive surface according to the present invention, not only the subtractive method but also the pattern plating/flash etching method can be used, and in either case, the overetching time can be set to a short time, so that the end faces of the obtained circuit are straighter and the cross section is closer to a rectangle. Therefore, it is a printed wiring board with excellent overall reliability, with excellent insulation reliability between circuits in a fine pattern, excellent signal transmission characteristics in high frequency regions flowing near the circuit surface due to the skin effect, and also resistant to noise such as crosstalk.

[0077]

In addition, the present invention provides a flexible printed wiring board characterized in that it was obtained using the aforementioned flexible copper-clad laminate. In manufacturing this printed wiring board, like the rigid printed wiring board described above, not only the subtractive method but also the pattern plating/flash etching method can be used. In either case, the overetching time can be set to a short time, so that the end faces of the obtained circuit are straighter and the cross section is closer to a rectangular shape. Therefore, it is a printed wiring board with excellent reliability and excellent signal transmission characteristics in high frequency regions, and it also does not generate noise such as crosstalk, and at the same time it has excellent insulation reliability and flexibility, and it is capable of demonstrating its advantage especially when it is a film carrier that directly mounts parts.

[0078]

Here, the above rigid copper-clad laminate or flexible copper-clad laminate (hereinafter referred to as simply "copper-clad laminate".) An example of a common processing method when machining a printed circuit board using any of the , is described for the avoidance of doubt. First, an etch resist layer is formed on the surface of the copper-clad laminate, the etch circuit pattern is exposed, developed, and an etch resist pattern is formed.

The etch resist layer at this time uses photosensitive resins such as dry films and liquid resists. In addition, UV exposure is common for exposure, and a method of forming an etch resist pattern based on a routine method can be employed.

[0079]

The electrolytic copper foil is then etched into a circuit shape using a copper etchant to form the desired circuit shape on the surface of the rigid or flexible substrate by performing etching resist peeling. With regard to etchants at this time, all copper etchants such as acidic copper etchants and alkaline copper etchants can be used.

[0080]

As described above, the copper-clad laminate according to the present invention is described as a concept that includes all of a single-sided copper-clad laminate, a double-sided copper-clad laminate, and a multilayer copper-clad laminate with an inner layer circuit. Therefore, in the case of a double-sided copper-clad laminate and a multi-layer copper-clad laminate, it may be necessary to ensure continuity between the layers, and in such cases, through holes, via holes, etc. are formed according to the standard method, and then continuity plating is performed to obtain interlayer continuity. Generally, this conductive plating process involves performing activation treatment using a palladium catalyst, followed by electroless copper plating,

and then developing the film thickness by electrolytic copper plating.

[0081]

When copper etching is completed, water washing is performed sufficiently, and rust prevention treatment, etc. is performed as necessary, such as drying, to become rigid printed wiring board or flexible printed wiring board.

[Examples of embodiments]

[0082]

Considering that the surface shape of the cathode does not affect the example compared to the example, the surface is polished with 2000 polishing paper, and the surface roughness is reduced to 0. Titanium plate electrodes adjusted to 85 μm were used.

[0083]

[Embodiment Group 1]

In this Embodiment Group 1, Embodiments 1 to 8 were implemented. In Embodiments 1 to 8, a copper sulfate solution having a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, and an MPS concentration, a DDAC polymer (Unisense FP A100L, manufactured by Senka Corporation), and a chlorine concentration as shown in Table 1 were used as the sulfuric acid-based copper electrolytic solution. In Embodiment 9, SPS, which is a binary of MPS, was used as an alternative to MPS.

[0084]

[Table 1]

Subject	Additive concentration (ppm)		
	MPS-Na	DDAC polymer	Chlorine
Embodiment 1	5	3	10
Embodiment 2	5	3	10
Embodiment 3	7	5	10
Embodiment 4	7	5	10
Embodiment 5	4	3	10
Embodiment 6	4	3	10
Embodiment 7	21	20	10
Embodiment 8	21	20	10
Embodiment 9	7*	5	10
: **: The MPS-Na concentration in Embodiment 9 is the equivalent value when SPS is used as Na salt			

[0085]

For the creation of electrolytic copper foil, DSA was used for the anode, electrolyzed at a liquid temperature of 50°C and current density of 60A/dm² to obtain nine electrolytic copper foil products of 12 μm and 210 μm thickness. The mechanical properties of the copper foil were evaluated only in this 12 μm electrolytic copper foil. The results are shown in Table 2.

[0086]

[Table 2]

	Copper foil thickness (μ m)	Electrolytic copper foil physical properties			
		Normal		After heating (180°C × 60 min.)	
		Tensile strength (kgf/mm ²)	Growth rate (%)	Tensile strength (kgf/mm ²)	Growth rate (%)
Embodiment 1	12	38.2	6.2	34.6	9.8
Embodiment 3	12	36.6	8.2	32.9	10.3
Embodiment 5	12	39.3	8.1	34.3	11.0
Embodiment 7	12	35.3	7.7	31.7	10.5
Embodiment 9	12	36.7	7.9	32.2	11.0
Comparative Example 1	12	36.2	4.0	32.4	5.6
Comparative Example 2	12	31.4	3.5	26.8	5.8
Comparative Example 3	12	40.5	3.6	39.5	4.4
Comparative Example 4	12	38.6	4.0	37.4	4.8

[0087]

The electrolytic copper foil was then subjected to rust prevention treatment on both sides. Here, inorganic rust prevention under the following conditions was adopted. A zinc sulfate bath was used to set the free sulfuric acid concentration at 70 g/l and the zinc concentration at 20 g/l, the liquid temperature was 40°C, the current density was 15 A/dm², and zinc anti-rust treatment was performed.

[0088]

Further, in the present embodiment, a chromate layer was formed electrolytically over the zinc rust-prevention layer. The electrolytic conditions at this time are as follows: chromic acid concentration 5.0 g/l, pH 11.5, liquid temperature 35°C, current density 8 A/dm², electrolysis time 5 seconds.

[0089]

After the rust prevention treatment was completed as described above, the silane coupling agent was immediately adsorbed on the rust prevention treatment layer on the precipitation surface in a silane coupling agent treatment tank. The solution composition at this time was γ -glycidoxypolytrimethoxysilane concentration of 5 g/l using pure water as the solvent. This solution was then adsorbed by spraying with a shower ring.

[0090]

Upon completion of the silane coupling agent treatment, the moisture was eventually dissipated by an electrothermal device to obtain nine types of surface treated electrolytic copper foil. According to the crystal structure analysis of the electrolytic copper foil obtained, the average crystal particle size was larger than the average crystal particle size of the electrolytic copper foil with a low profile due to the fine crystallization used in conventional film carrier tapes, and the presence of twin crystals was also confirmed. The surface roughness (Rzjis) and gloss [Gs(20°)], [Gs(60°)] and [Gs(85°)] of the deposit side of the electrolytic copper foil obtained above, and the surface roughness (Rzjis) and gloss [Gs(60°)] of the deposit side of the surface-treated electrodeposited copper foil are shown in Table 3.

[0091]

[Table 3]

	Copper Foil Thickness (μm)	Electrolytic copper foil								Surface treated copper foil		
		Precipitation surface								Precipitation surface		
		Rzjis (μm)	Gloss							Rzjis (μm)	Gloss	
			Gs (20°)		Gs (60°)			Gs (85°)			Gs (60°)	
			TD	MD	TD	MD	TD/MD	TD	MD		TD	MD
Embodiment 1	12	0.30	844	988	652	675	0.97	129	138	0.32	621	647
Embodiment 2	210	0.27	1169	1263	624	661	0.94	124	129	0.33	592	602
Embodiment 3	12	0.33	910	970	647	673	0.96	129	140	0.29	597	613
Embodiment 4	210	0.29	1074	1144	656	670	0.98	115	128	0.36	546	547
Embodiment 5	12	0.35	718	838	643	660	0.97	123	138	0.33	581	602
Embodiment 6	210	0.34	1147	1182	631	662	0.95	112	119	0.36	587	582
Embodiment 7	12	0.33	941	1043	650	677	0.96	132	142	0.30	606	611
Embodiment 8	210	0.30	1223	1271	661	692	0.96	118	124	0.32	576	576
Embodiment 9	12	0.34	800	824	650	674	0.96	117	133	0.32	618	623
Comparative Example 1	12	0.85	-	-	-	283	-	-	-	-	-	-
	210	0.70	-	-	-	221	-	-	-	-	-	-
Comparative Example 2	12	0.83	-	-	-	374	-	-	-	-	-	-
	210	1.22	-	-	-	386	-	-	-	-	-	-
Comparative Example 3	12	3.60	-	-	-	0.7	-	-	-	-	-	-
Comparative Example 4	12	3.59	-	-	-	1.0	-	-	-	-	-	-

[0092]

[Embodiment Group 2]

Here, Embodiments 10 to 14 used a solution adjusted to a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, and a concentration of SPS as described in Table 4, a DDAC polymer (unisense FPA 100 L made of Senka (strain)), and a chlorine concentration as sulfate-based copper electrolyte.

[0093]

[Table 4]

	Additive concentration (ppm)		
	SPS-Na	DDAC polymer	Chlorine
Embodiment 10	5	30	25
Example 11	10	20	22
Example 12	100	100	100
Example 13	50	70	100
Example 14	50	100	50

[0094]

The creation of electrolytic copper foil was electrolyzed using a DSA on the anode at a liquid temperature of 50°C and a current density of 60 A/dm², and two electrolytic copper foil products of 12 μm and 70 μm thickness were obtained in Example 10 and four electrolytic copper foil products of 12 μm thickness were obtained in Examples 11-14.

[0095]

The normal state of the 12 μm and 70 μm electrolytic copper foil obtained in Example 10 and 180°C x 60 min. The tensile strength and elongation rate after heating are shown in Table 5. The tensile strength of the 12 μm electrolytic copper foil in question is 35. 5 kgf/mm², growth rate 11. 5%, 180°C x 60 min. The tensile strength after heating is 33. 2 kgf/mm², 11. The favorable mechanical properties of 2% are at levels that are sufficient to withstand the folding use of flexible printed circuit boards.

[0096]

[Table 5]

	Copper foil thickness (μm)	Normal		180°C $\times$ 60 min. After heating	
		Tensile strength	Growth Rate	Tensile strength	Growth Rate
		Kgf/mm ²	%	Kgf/mm ²	%
Example 10	12	35.5	11.5	33.2	11.2
	70	34.4	28.0	32.3	31.8
Comparative Example 1	12	37.9	8.0	31.6	7.5

[0097]

When evaluating the fold resistance of the above 12 μm electrolytic copper foil alone by MIT method, it is able to withstand folding tests of 1,200 to 1,350 times and 800 to 900 times even after heating. The fold resistance test according to the above MIT method uses a film fold resistance test machine with tank made by Toyo Seiki Corporation (part number: 549) as the MIT fold resistance device, and the bending radius is 0.8 mm, load 0.5 kgf and sample size 15 mm $\times$ 150 mm. This number is approximately 600 times normal when evaluating general-purpose electrolytic copper foil used in conventional flexible printed wiring board applications under the same conditions, and 500 times after heating, so it shows approximately twice the fold resistance of conventional general-purpose products. It can be inferred that this difference is due to the effect that the smooth surface is less likely to cause cracks that can lead to fracture.

[0098]

Then, the electrolytic copper foil obtained above was immersed in a dilute sulfuric acid solution at a concentration of 150 g/l and a liquid temperature of 30°C for 30 seconds, and the deposits and surface oxidative film were removed and washed with water. For the 12 μm electrolytic copper foil and 70 μm electrolytic copper foil obtained in Example 10, a total of four types of surface treated electrolytic copper foil and two types of surface treated electrolytic copper foil without roughening were created, respectively.

[0099]

The 12 μm electrolytic copper foil and 70 μm electrolytic copper foil that are subject to roughening treatment above were subjected to the process of precipitation and deposition of fine copper particles on the precipitation surface as a process of forming fine copper particles on the precipitation surface of the electrolytic copper foil when the acid washing process is completed, and the coating process was applied to prevent the dropping of these fine copper particles. In the process of precipitating and adhering the fine copper grains of the former, a copper sulfate-based solution was electrolyzed for 5 seconds under the conditions of copper concentration 15 g/l, free sulfuric acid concentration 100 g/l, liquid temperature 25°C, and current density 30 A/dm².

[0100]

When fine copper particles were adhered to the precipitation surface, copper was evenly precipitated to cover the fine copper particles under smooth plating conditions as a coating plating process to prevent the removal of the fine copper particles. Here, as the smooth plating conditions, the copper sulfate solution was set to a copper concentration of 60 g/l, a free sulfuric acid concentration of 100 g/l, a liquid temperature of 45°C, and a current density of 45 A/dm², and electrolyzed for 5 seconds.

[0101]

In this example, rust prevention treatment was performed on both sides of all electrolytic copper foil obtained, and inorganic rust prevention was adopted in this case under the conditions described below. A zinc sulfate bath was used to set the free sulfuric acid concentration at 70 g/l and the zinc concentration at 20 g/l, the liquid temperature was 40°C, the current density was 15 A/dm², and zinc anti-rust treatment was performed.

[0102]

The chromate layer was further electrolytically formed over the zinc rust prevention layer. The electrolytic conditions at this time are as follows: chromic acid concentration 5.0 g/l, pH 11.5, liquid temperature 35°C, current density 8 A/dm², electrolysis time 5 seconds.

[0103]

After the rust prevention treatment was completed as described above, the silane coupling agent was immediately adsorbed on the rust prevention treatment layer on the precipitation surface in a silane coupling agent treatment tank. The solution

composition at this time was such that pure water was used as a solvent and the concentration of γ -glycidoxypolytrimethoxysilane was

5 g/l. This solution was then adsorbed by spraying with a shower ring. When the silane coupling agent treatment was finished, the water was eventually dissipated by an electrothermal device to obtain six types of surface treated electrolytic copper foil, including one type of roughening treatment foil.

[0104]

Table 6 shows the surface roughness (Rzjis) and gloss [Gs (60°)] on the glossy side of the electrolytic copper foil obtained from Examples 10-14 above, the surface roughness (Gs (20°)) and gloss [Gs (60°)] on the precipitated side, [Gs (60°)] and [Gs (85°)], and the surface roughness (Gs (60°)) on the precipitated surface of the surface treated foil obtained from Example 10, and the surface roughened surface roughened surface (Rzjis).

[0105]

[Table 6]

	Copper foil thickness (μm)	Electrolytic copper foil											Surface treated copper foil			
		Glossy surface			Precipitation surface								Precipitation surface			Roughening surface
		Gloss Gs (60°)		Rzjis (μm)	Gloss Gs (20°)		Light intensity Gs (60°)			Gloss Gs (85°)		Rzjis (μm)	Gloss Gs (60°)		Rzjis (μm)	
		TD	MD		TD	MD	TD	MD	TD/MD	TD	MD		TD	MD		
Embodiment 10	12	165	311	0.87	1027	1058	659	665	0.99	142	139	0.32	540	514	0.28	0.97
	70	140	291	0.84	1510	1506	691	686	1.01	149	150	0.17	570	570	0.15	-
Example 11	12	157	294	1.14	925	1206	735	759	0.97	114	112	0.30	-	-	-	-
Example 12	12	158	279	0.91	823	976	613	651	0.94	98	118	0.39	-	-	-	-
Example 13	12	159	295	0.97	800	955	603	665	0.91	116	129	0.41	-	-	-	-
Example 14	12	158	295	1.02	867	968	627	649	0.97	114	129	0.32	-	-	-	-
Comparative Example 1	12	150	260	1.14	116	126	324	383	0.85	111	117	1.00	150	260	0.98	1.70

[Comparative Example]

[0106]

[Comparative Example 1]

This comparative example is the trace experiment of Example 1 described in Patent Reference 2. As a sulfate-based copper electrolyte, the basic solution was dissolved in pure water with copper sulfate (reagent) and sulfuric acid (reagent), and the concentration of copper sulfate (5-hydrate conversion) was 280 g/l, and the concentration of free sulfuric acid was 90 g/l. Then, the copolymer of diallyl dialkylammonium salt and sulfur dioxide (manufactured by Nitto Spine Co., Ltd., trade name PAS-A-5, weight average molecular weight 4000) concentration was adjusted to 4 ppm, polyethylene glycol (average molecular weight 1000) concentration to 10 ppm, and MPS-Na concentration to 1 ppm, and furthermore, sodium chloride was used to prepare the chlorine concentration to 20 ppm as the sulfate acid copper plating solution.

[0107]

The anode was electrolyzed using a lead plate at a liquid temperature of 40°C and a current density of 50 A/dm² to obtain electrolyzed copper foils of 12 μm and 210 μm thickness. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and gloss [Gs (60°)] of the precipitate surface are shown in Table 3, along with examples.

[0108]

[Comparative Example 2]

In this comparative example, a solution with a copper concentration of 90 g/l and a free sulfuric acid concentration of 110 g/l was cleaned through an activated carbon filter as a sulfate-based copper electrolyte. Copper electrolytes were then added to this solution so that the concentration of MPS-Na was 1 ppm, the concentration of hydroxyethylcellulose was 5 ppm, the concentration of low molecular weight gut (number average molecular weight 1560) was 4 ppm, and the concentration of chlorine was 30 ppm as polymeric polysaccharides. Using the copper electrolyte prepared in this manner, electrolysis was performed using a DSA electrode on the anode at a liquid temperature of 58°C and a current density of 50 A/dm² to obtain electrolytic copper foil products with a thickness of 12 μm and 210 μm. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and glossiness of the precipitated surface, etc., are shown in Table 3 together with the examples.

[0109]

[Comparative Example 3]

In this comparative example, electrolysis was performed using a sulfuric acid-based copper electrolytic solution having a

copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, a DDAC polymer (Unisense FPA100L, manufactured by Senka Corporation) concentration of 4 ppm, and

A solution with a prime concentration of 15 ppm was used. a DSA electrode as the salt anode at a solution temperature of 50° C, and a current density of 60 A/dm² to obtain an electrolytic copper foil having a thickness of 12 μm. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and glossiness of the precipitated surface, etc., are shown in Table 3 together with the examples.

[0110]

[Comparative Example 4]

In this comparative example, the sulfuric acid-based copper electrolyte used had a copper concentration of 80 g/l, a free sulfuric acid concentration of 140 g/l, a DDAC polymer (Unisense FPA100L, manufactured by Senka Corporation) concentration of 4 ppm, a low molecular weight glue (number average molecular weight 1560) concentration of 6 ppm, and a chlorine concentration of 15 ppm. The anode was electrolyzed using a DSA electrode at a liquid temperature of 50°C and a current density of 60 A/dm² to obtain an electrolytic copper foil with a thickness of 12 μm. The mechanical properties of this electrolytic copper foil are shown in Table 2, and the surface roughness (Rzjis) and gloss [Gs (60°)] of the precipitate surface are shown in Table 3, along with examples.

[0111]

[Comparative Example 5]

This comparative example is the trace experiment of Embodiment 1 described in Patent Reference 2. The basic solution of the sulfate-based copper electrolyte was dissolved in pure water with copper sulfate (reagent) and sulfuric acid (reagent), and the concentration of copper sulfate (5-hydrate conversion) was 280 g/l, and the concentration of free sulfuric acid was 90 g/l. This was adjusted to 4 ppm for the copolymer (manufactured by Nitto Tosei Co., Ltd., trade name PAS-A-5, weight average molecular weight 4000), 10 ppm for the polyethylene glycol (average molecular weight 1000), and 1 ppm for the MPS-Na concentration, and 20 ppm for the chlorine concentration using sodium chloride.

[0112]

The anode was electrolyzed using a lead plate at a liquid temperature of 40°C and a current density of 50 A/dm² to obtain electrolyzed copper foil with a thickness of 12 μm and 70 μm, and then two types of surface-treated electrolyzed copper foil were obtained in the same manner as Example 10. The normal state of this electrolytic copper foil and 180°C × 60 min. The mechanical properties after heating are shown in Table 5, and the surface roughness (Rzjis), gloss [Gs (20°)], [Gs (60°)], and [Gs (85°)], surface roughness (Rzjis) and gloss [Gs (60°)], and roughening surface (Rzjis) of the roughening treated foil are shown in Table 6.

[0113]

[Comparison with Embodiments and Comparative Examples]

Each comparative example and embodiment will be compared and the results will be described below. The precipitation surface side of the electrolytic copper foil obtained in the example is surface roughness (Rzjis) < 1.0 μm, gloss [Gs (60°)] ≥ 400 and its TD/MD ratio is 0.9 - 1.1 and [Gs (20°)] > [Gs (60°)] > [Gs (85°)] In addition, the mechanical properties of the normal state also satisfy the conditions of the present invention, where the tensile strength is 33 kgf/mm² or more and the elongation rate is 5% or more, and the mechanical properties after heating are 30 kgf/mm² or more and the elongation rate is 8% or more.

[0114]

Comparative to Comparative Example 1: Comparatively comparing the surface roughness (Rzjis) of the precipitation surface side of the electrolytic copper foil, the electrolytic copper foil of Comparative Example 1 also has a favorable low profile. However, the surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil incorporated into the present invention is 0.30 μm to 0. The surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil in Comparative Example 1 was 0. The surface roughness (Rzjis) of the precipitation surface of 85 μm and 210 μm electrolytic copper foil incorporated into the present invention is 0.27 μm to 0. The surface roughness (Rzjis) of the precipitation surface of the 210 μm electrolytic copper foil in Comparative Example 1 is 0. It is 70 μm. Therefore, while there is a common tendency for a smoother precipitation surface to be obtained as the copper foil thickness increases, the electrolytic copper foil incorporated into the present invention is superior in the absolute value of smoothness. Also, when comparing the gloss [Gs (60°)], the gloss [Gs (60°)] of Comparative Example 1 is in the range of 221 to 283, whereas the gloss [Gs (60°)] of

each example shows a completely different range of 603 to 759. Based on this, compared to the electrolytic copper foil of Comparative Example 1, it can be said that each electrolytic copper foil of the Example has a flatter, closer precipitation surface to the mirror surface. As for the mechanical properties,

the 12 μm electrodeposited copper foil of Comparative Example 1 had a tensile strength of 36.2 kgf/mm², elongation rate 4.0%, tensile strength after heating 32.4 kgf/mm², 5.6%, which is equivalent to the electrolytic copper foil of the example is the tensile strength in normal conditions.

[0115]

Comparison between Embodiment and Comparative Example 2: Comparing the surface roughness (Rzjis) of the deposit side of the electrolytic copper foil, the electrolytic copper foil of Comparative Example 2 also has a good low profile. However, the surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil incorporated into the present invention is 0.30 μm to 0. The surface roughness (Rzjis) of the precipitation surface of the 12 μm electrolytic copper foil in Comparative Example 2 was 0. The surface roughness (Rzjis) of the precipitation surface of 83 μm and 210 μm electrolytic copper foil incorporated into the present invention is 0.27 μm to 0. Compared to 34 μm , the surface roughness (Rzjis) of the precipitation surface of the 210 μm electrolytic copper foil in Comparative Example 2 was 1. It is 22 μm . Therefore, in Comparative Example 2, it is considered difficult to obtain a stable and smooth electrolytic copper foil because the smoothness of the precipitation surface is impaired by increasing the copper foil thickness. And with regard to mechanical properties, the 12 μm electrolytic copper foil of Comparative Example 2 is normally 31.4 kgf/mm², elongation rate 3.5%, tensile strength after heating 26.8 kgf/mm², 5.8%, and each electrolytic copper foil of the example is superior.

[0116]

Comparison with Embodiment and Comparative Example 3: Comparative Example 3 is for looking at the effect of the absence of MPS or SPS in the copper electrolyte. As is clear from Table 3, the surface roughness (Rzjis) of the precipitation surface of the electrolytic copper foil obtained in Comparative Example 3 without MPS, etc. in the copper electrolyte solution is 3. It shows 60 μm , and low profile has not been achieved. And since the gloss [Gs (60°)] is almost matte, it is 0.7 and very low. The mechanical properties of 12 μm electrolytic copper foil have a tensile strength of 40. Although it shows a large value of 5 kgf/mm², the elongation rate is 3. It is 6% lower and the change due to heating is small. Therefore, it can be said that the electrolytic copper foil incorporated into the present invention is superior in terms of surface roughness and elongation rate.

[0117]

Comparison with Embodiment and Comparative Example 4: Comparative Example 4 sees the effect of adding a small molecule plaster instead of MPS to the copper electrolyte. As a result, as can be clearly seen from Table 3, even if a small molecule plaster is included in the copper electrolyte instead of MPS, the surface roughness (Rzjis) of the precipitation surface of the electrolytic copper foil is 3.59 μm is shown, and low profile has not been achieved. And since the degree of gloss [Gs (60°)] is almost matte, 1. It shows a very low value of 0. In terms of mechanical properties, the tensile strength of the normal state is 38.6 kgf/mm² and the same value as the example, but the elongation rate is 4.0%, and as in Comparative Example 3, the change due to heating is small. Therefore, it can be said that the electrolytic copper foil incorporated into the present invention is superior in terms of surface roughness and elongation rate.

[0118]

Embodiment vs. Comparative Example 5: Example vs. Comparative Example 5 is compared between 12 μm electrolytic copper foil products with reference to the data described in Table 5 and Table 6 hereinafter.

[0119]

Comparing the surface roughness (Rzjis) on the precipitation surface side, the electrolytic copper foil obtained in the example is 0.30 μm to 0.41 μm , the electrolytic copper foil obtained in Comparative Example 5 has a surface roughness (Rzjis) of the deposit side of 1. The difference between 00 μm and that is clear. The glossiness of the precipitation surface alone [Gs (60°)] is in the range of 324 to 383 for the electrolytic copper foil obtained in Comparative Example 5, whereas the electrolytic copper foil obtained in the Embodiments is in the completely different range of 603 to 759. That is, compared to the electrolytic copper foil of Comparative Example 5, the electrolytic copper foil of the example has a flatter and closer to the mirror surface. As for the mechanical properties in the normal state, the electrodeposited copper foil of Comparative Example 5 had a tensile strength of 37.9 kgf/mm², an elongation of 8.0%, while the electrodeposited copper foil of Example 10 had a tensile strength of 35.5 kgf/mm², and an elongation of 11. [missing text] 5%, which showed that the foil was somewhat more

flexible. 180°C x 60 min. The mechanical properties after heating are as follows: the tensile strength of the electrolytic copper foil of Comparative Example 5 is 31.6 kgf/mm², the elongation of 7. had a tensile strength of 31.6 kgf/mm² and an elongation of 7.5%, while the electrodeposited copper foil of Example 10 had a tensile strength of 33.2 kgf/mm², and the elongation of 11. [missing text] 2%, showing that the electrodeposited copper foil

of the present invention is superior. Based on these results, considering the heat history when processed into a copper-clad laminate plate, it is possible to expect excellent flex resistance, etc., when using a flexible printed wiring plate using, for example, electrolytic copper foil incorporated into the present invention.

[0120]

Next, we confirmed the superiority of using three types of gloss as an indicator of surface uniformity. When looking at the difference in glossiness with MD as the common direction at the precipitation plane of the 12 μ m electrolytic foil obtained in the examples, [Gs (20°)] is 824 to 1206, [Gs (60°)] is 649 to 759, and [Gs (85°)] is 112 to 142, which is larger as the angle of incidence of the measured light approaches vertically. In contrast, looking at the evaluation results obtained in Comparative Example 5, when measured in the MD direction on the precipitation surface side of 12 μ m electrolytic copper foil, [Gs (20°)] is 126, [Gs (60°)] is 383, and [Gs (85°)] is 117, and [Gs (20°)] and [Gs (85°)] are almost equivalent. Therefore, the precipitation surface of the 12 μ m electrolytic copper foil obtained in Comparative Example 5 has some characteristic shape.

[0121]

Therefore, the SEM photograph of the 12 μ m electrolytic copper foil precipitation surface obtained in Embodiment 11 is shown in Figure 1, and the SEM photograph of the 12 μ m electrolytic copper foil precipitation surface obtained in Comparative Example 5 is shown in Figure 2. As is clear from Figure 2, in addition to small unevenness being observed on the electrolytic copper foil surface obtained in Comparative Example 5, abnormal precipitation areas that cannot be detected without observation at high magnification are also occasionally observed. That is, the diffuse reflection of light in this uneven part reduces the value of the gloss [Gs (20°)] and increases the surface roughness (Rzjis). In addition, no obvious unevenness was observed in Figure 1, which is an SEM photograph of electrolytic copper foil incorporated into the present invention, and no abnormal precipitation area was observed. Therefore, the electrolytic copper foil according to the present invention has excellent uniform surface roughness and gloss.

[0122]

And when comparing the roughening treated surface treated electrolytic copper foil, in contrast to Embodiment 10 and Comparative Example 5, the increase in the value of surface roughness (Rzjis) due to the roughening treatment performed under the same conditions was approximately 0.7 μ m, which is almost the same. As can be seen from Figure 2, the irregularities seen in the precipitation surface shape of the electrolytic copper foil obtained in Comparative Example 5 have a pitch of around 3 μ m, but are flat, so it can be inferred that the fine particles obtained from the roughening process adhere along the respective irregularities. However, in the electrolytic copper foil of Comparative Example 5, the surface roughness (Rzjis) of the adhesive surface with the insulating layer component material that is the requirement of the present invention is large because of the surface roughness (Rzjis) of the precipitation surface that is the base. It cannot be less than 5 μ m, and the superiority of the electrolytic copper foil pertaining to the present invention is clear.

[0123]

Comparison between MPS and SPS: Examples 9 to 14 use SPS as an alternative to MPS, but the resulting 12 μ m electrolytic copper foil has a surface roughness (Rzjis) of 0.30 μ m to 0. The 41 μ m gloss [Gs (60°)] ranged from 603 to 759, confirming that SPS can have the same effect as MPS.

[0124]

In the above example, when making the electrolytic copper foil incorporated into the present invention, favorable results are obtained with the solution configuration with the copper concentration of the sulfate-based copper electrolyte at 40 g/l to 120 g/l and the free sulfuric acid concentration at 60 g/l to 220 g/l, but it is acceptable to change the concentration range according to the intended application. In addition, the presence of additives other than the additives described in the above examples is not denied, and if it has been confirmed that the effects of the above additives can be further enhanced or contributed to the quality stabilization during continuous production, it is acceptable to add them voluntarily.

[Industrial Availability]

[0125]

The precipitation surface of the electrolytic copper foil obtained using the method for producing the electrolytic copper foil related to the present invention has a lower profile than the low profile electrolytic copper foil supplied to the conventional market, and the roughness of the precipitation surface is less than the roughness of the gloss surface, resulting in a glossy smooth surface on both sides. The copper electrolyte used in the production of electrolytic foil

has a high adaptability to variations in manufacturing conditions and thickness, and is therefore highly productive. Thus, it is suitable for forming fine pitch circuits of tape automatic bonding (TAB) substrates and chip-on-film (COF) substrates, as well as electromagnetic shielding circuits of plasma display panels. In addition, this electrolytic copper foil has excellent mechanical properties, making it suitable for use as a current collector that constitutes a negative electrode, such as a lithium ion secondary battery.

[Brief description of the drawings]

[0126]

[Fig. 1] SEM photograph of the 12 μm electrolytic copper foil precipitation surface obtained in Example 11.

[Fig. 2] This is an SEM photograph of the 12 μm electrolytic copper foil precipitation surface obtained in Comparative Example 5.

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(72) Inventor Makoto Tsuchihashi
1333-2 Haraichi, Ageo-shi, Saitama Prefecture Mitsui Mining & Smelting Co., Ltd. Research Institute

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