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(54) METHOD FOR MANUFACTURING VERY LOW ROUGHNESS ELECTRODEPOSITED COPPER FOIL AND ELECTRODEPOSITED COPPER FOIL MANUFACTURED THEREBY

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(57) **ABSTRACT**

The present invention relates to a method for manufacturing a low roughness electrodeposited copper foil, and an electrodeposited copper foil manufactured thereby, and uses an electrolyte which basically consists of a sulfuric acid, a copper ion and a chloride ion is adapted with an additive which consists of a HEC (Hydroxyethyl Cellulose) of 0.05~50 ppm, a SPS (bis(sodiumsulfopropyl)disulfide) of 0.05~20 ppm, and a gelatin of 0.1~100 ppm. The present invention is adapted to manufacture a low roughness electrodeposited copper foil using a conventional copper foil manufacture facility and the electrodeposited copper foil according to the present invention is adapted as a material for a copper clad laminate for a printed circuit substrate and an electrode material for a lithium ion battery.

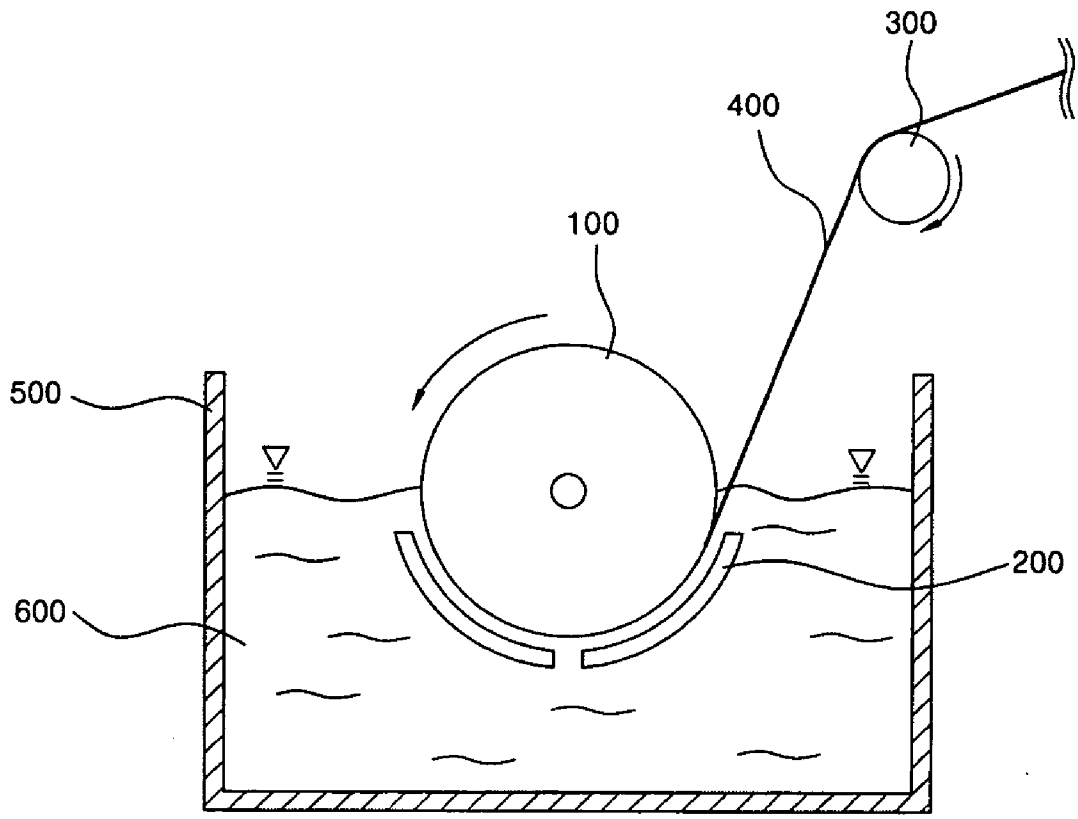

FIG. 1

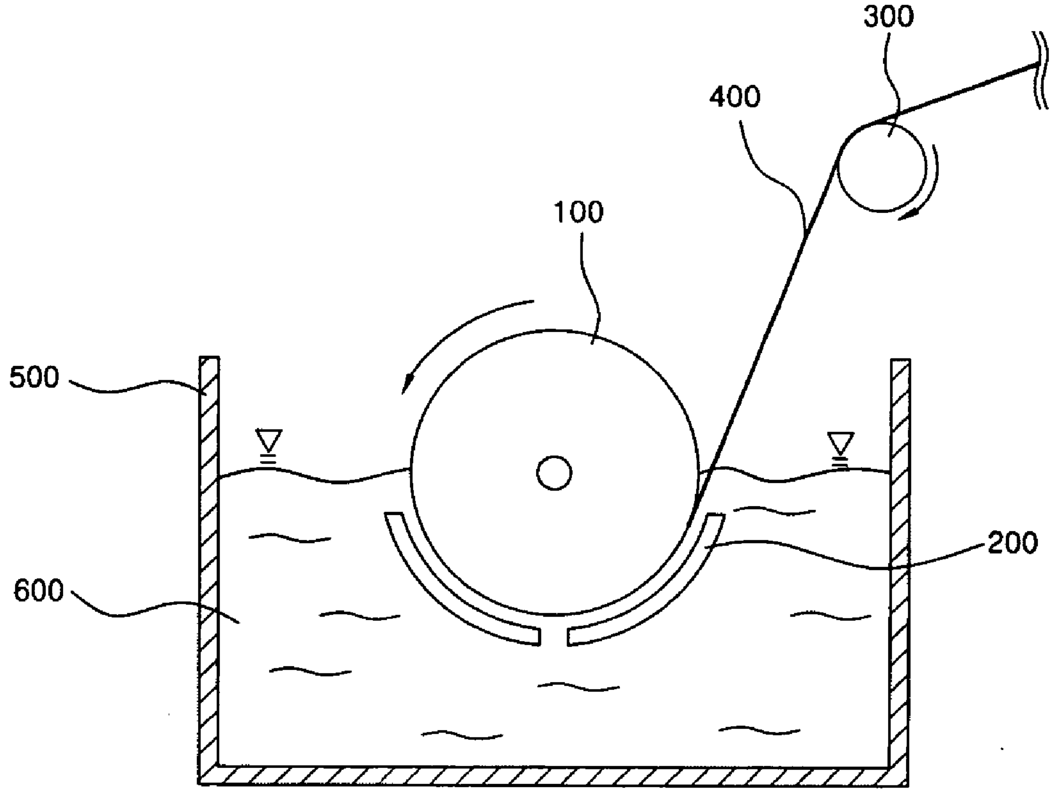

FIG. 2

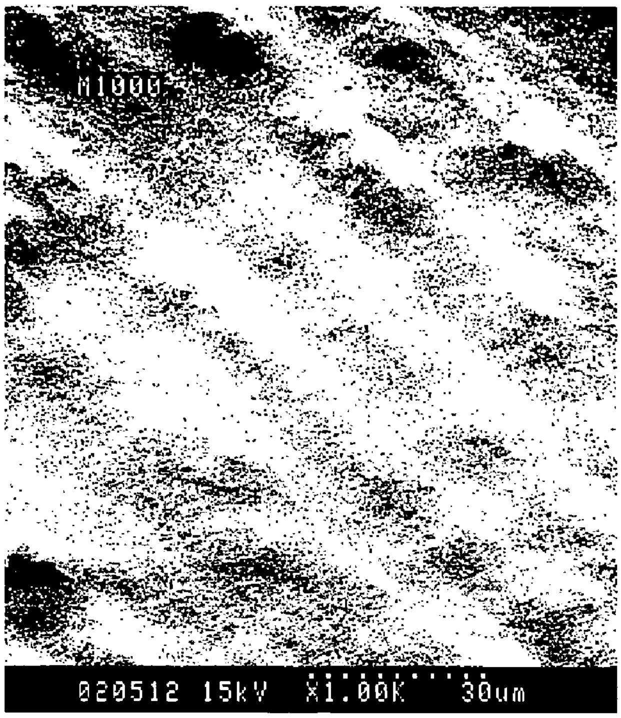

FIG. 3

METHOD FOR MANUFACTURING VERY LOW ROUGHNESS ELECTRODEPOSITED COPPER FOIL AND ELECTRODEPOSITED COPPER FOIL MANUFACTURED THEREBY

RELATED U.S. APPLICATIONS

[0001] Not applicable.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

REFERENCE TO MICROFICHE APPENDIX

[0003] Not applicable.

FIELD OF THE INVENTION

[0004] The present invention relates to a method for manufacturing an electrodeposited copper foil adhered to a prepreg for a PCB(Printed Circuit Board) and an electrodeposited copper foil manufactured thereby, and in particular to a method for manufacturing an electrodeposited copper foil which does not have a residual copper by decreasing a roughness of a matte side of an electrodeposited copper foil even when a fine pattern is formed.

BACKGROUND OF THE INVENTION

[0005] Generally, a PCB is widely used in a home appliance such as a radio, television, washing machine, VCR, etc., and an industrial electric/electronic instrument such as a computer, wireless communication instrument, various controllers, etc. The PCB is formed of an insulated substrate such as a prepreg of a frame retardant formed in such a manner that a glass fiber is impregnated in foil is adhered to an insulation substrate at a high temperature and pressure, and then the electrodeposited copper foil is etched based on a circuit design.

[0006] The electrodeposited copper foil adhered to the insulation substrate is manufactured by the following processes. A raw foil is manufactured in a copper sulphate solution by a continuous electrodepositing method. Next, a nodule process is performed with respect to a raw copper foil for forming a copper nodule for thereby enhancing an adhesion to an insulation substrate and a barrier layer is formed on the copper foil surface. Finally, a corrosion resist chromating process is performed.

[0007] Recently, as an electric/electro instrument is made thin, a printed circuit for a substrate need have a fine and high intensive and compact construction. For this, a method for developing a very low roughness copper foil has been provided.

[0008] In a conventional electrodeposited copper foil manufacturing method, a first method is to divide an electrolytic section into two sections and then to enhance a current density of a second section rather than a first section for thereby obtaining a low roughness copper foil.

[0009] A super anode is attached to a foil manufacturing apparatus of the above manufacturing facility. In the case that the super anode is adapted, it is possible to change the size of a nucleus when a nucleus is initially generated by adjusting the current applied to the super anode and the main anode. Therefore, it is possible to manufacture the low roughness copper foil by accurately adjusting the size of the initial nucleus. However, it is impossible to manufacture a low roughness copper foil corresponding to the recent fine circuit pattern with the above described method.

[0010] A second method is directed to decreasing the concentration of a chloride ion in an electrolyte below 1 ppm for thereby obtaining a low roughness copper foil. However, it is possible to decrease the concentration of a chloride ion below 1ppm based on only an experimental condition. In the case that the electrodeposited copper foil is manufactured, a copper scrap is generally used as a source material. When the copper scrap is used for the mass production system, there is no suitable economic method for preventing a chloride ion generated by a waste electric wire. Therefore, it is impossible to implement an actual practicality.

[0011] A third method is directed to obtaining a low roughness copper foil by mechanically polishing a conventional electrodeposited copper foil through a buffing method. However, the above method is needed to have an additional manufacturing facility. If there is a surplus during the buffing process, a residual copper may be formed during the manufacture of the PCB.

[0012] A fourth method is directed to adjusting morphology of a copper foil by changing an additive added to an electrolyte. In more detail, the above fourth method is directed to implementing a low roughness copper foil by adding a low molecular weight water-soluble cellulose ether, a low molecular weight water-soluble polyalkylene glycol ether, a low molecular weight water-soluble polyethyleneimine, and a water soluble sulfonated organic sulfur compound. In the above method, it is possible to manufacture a low roughness copper foil by changing only an additive of an electrolyte without changing or modifying a conventional copper manufacture apparatus. In addition, a mechanical polishing process like a buffing process is not needed. It is not needed to manage a chloride ion at a very low degree. The above method is more economical compared to the other methods.

[0013] However, since the copper foil manufactured by the above method has a roughness Rz of a matte side of 3.81 μm, the above method does not satisfy the demand of the recent low roughness copper foil.

[0014] A fifth method is directed to manufacturing a low roughness copper foil using an electrolyte including a small amount of polyethylene glycol, tin ion, iron ion and a chloride ion of below 0.1 ppm. In the above method, there is a limit for substantially maintaining the concentration of the chloride ion below 0.1 ppm for a mass production.

BRIEF SUMMARY OF THE INVENTION

[0015] Accordingly, it is a first object of the present invention to provide a method for manufacturing a low roughness electrodeposited copper foil and an electrodeposited copper foil manufactured by the method which does not need a design change or modification of a conventional copper manufacture apparatus and directly uses a source material of a low cost waste electric wire without using a conventional facility like a mechanical polishing apparatus and an additional process and is capable of manufacturing an electrodeposited copper foil having a low roughness by adjusting the amount of an additive.

[0016] It is a second object of the present invention to provide a method for manufacturing a low roughness electrodeposited copper foil and an electrodeposited copper foil manufactured by the same which are well adapted to an electrode of a lithium ion battery or copper clad laminates which is used in an electronic instrument such as a PCB and a flexible circuit substrate, etc.

[0017] To achieve the above objects, in a method for manufacturing an electrodeposited copper foil in which a rotating drum and an anode plate formed of a curve distanced from an outer surface of the drum by a certain distance are drowned in an electrolyte, said electrolyte consists of a sulfuric acid, copper ion and chloride ion, and an electrodeposited copper foil is deposited on a surface of the drum as a negative current is applied to the drum and a positive current is applied to the anode plate, there is provided a method for manufacturing an electrodeposited copper foil which is characterized in that an additive which consists of a gelatin of 0.1~100 ppm, a HEC(Hydroxyethyl Cellulose) of 0.05 ppm~50 ppm, and a SPS(bis(sodiumsulfopropyl)disulfide) of 0.05~20 ppm is added to the electrolyte.

[0018] The amount of the addition of the gelatin is preferably 2~5 ppm. The amount of the addition of the HEC is preferably 1~3 ppm. The amount of the addition of the SPS is preferably 0.5~3 ppm.

[0019] The molecular weight of the gelatin is preferably above 10000.

[0020] There is preferably further provided a post-treatment for forming a nodule on one surface or both surfaces of the electrodeposited copper foil.

[0021] A roughness of a matte side of the electrodeposited copper foil is larger than that of a shiny side.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0022] The present invention will become better understood with reference to the accompanying drawings which are given only by way of illustration and thus are not limitative of the present invention, wherein;

[0023] **FIG. 1** is a view illustrating the construction of a copper manufacture apparatus for describing a method for manufacturing an electrodeposited copper foil according to the present invention;

[0024] **FIG. 2** is a picture obtained by photographing an electrodeposited copper foil manufactured according to an embodiment **1** of the present invention using a SEM; and

[0025] **FIG. 3** is a picture obtained by photographing an electrodeposited copper foil manufactured according to a comparison example 2 using a SEM.

DETAILED DESCRIPTION OF THE INVENTION

[0026] **FIG. 1** is a view illustrating a copper foil manufacture apparatus for describing a method for manufacturing an electrodeposited copper foil according to the present invention.

[0027] As shown in **FIG. 1**, the copper foil manufacture apparatus is constructed in such a manner that a rotating drum **100** and a circular shaped anode plate **200** are spaced apart by a certain distance. Here, the drum **100** and the anode plate **200** are provided within a tank **500** having an electrolyte **600**.

[0028] Here, a lower portion of the rotation center of the drum **100** is drowned in the electrolyte **600**. The anode plate **200** is drowned in the electrolyte **600** in such a manner that the drowned shape of the drum **100** corresponds to the drowned shape of the anode plate **200**. The negative and positive currents are applied to the drum **100** and the anode plate **200**, respectively.

[0029] Preferably, the electrolyte **600** filled in the tank **500** consists of H_2SO_4 of about 50~200 g/l, Cu^{2+} of about 30~150 g/l, and Cl^- of below about 200 mg/l. The temperature of the electrolyte **600** is about 20~80° C., and the current density is about 20~150 A/dm^2.

[0030] An electrolytic process is performed between the drum **100** and the anode plate **200**, such that an electrodeposited copper foil **400** is deposited on a surface of the drum **100**. The electrodeposited copper foil **400** is rolled up by the roller **300** installed in the upper right side.

[0031] A certain additive is usually provided into the electrolyte **600** for adjusting a material property of the electrodeposited copper foil **400** in the above method. In the present invention, the electrodeposited copper foil **400** having a fine circuit pattern is manufactured by using a gelatin, and HEC(Hydroxyethyl cellulose), SPS(bis(sodiumsulfopropyl)disulfide) as an additive. In addition, a low roughness electrodeposited copper foil **400** which may be used as an electrode material of a lithium ion battery is manufactured.

[0032] The gelatin used as an additive is a kind of a drived protein and has a molecular weight of above 10000. If the gelatin having molecular weight below 10000 is used, an interaction between SPS and HEC is weakened, so that an electrodeposited copper foil having ununiform roughness and gloss is manufactured. In the case that the molecular weight of the gelatin is above 10000, it is possible to manufacture a low roughness copper foil having a uniform roughness and gloss.

[0033] The amount of the addition of the gelatin is minimum about 0.1 ppm through maximum about 100 ppm. Preferably, the amount range of the addition of the gelatin is about 1~10 ppm. More preferably, the amount range of the same is about 2~5 ppm.

[0034] If the gelatin is added below 0.1 ppm in the electrolyte **600**, more delicate initial structure may be obtained, but an electrodeposited copper foil with high roughness is obtained by promoting the growth of the copper foil **400**. Accordingly, an electrodeposited copper foil with low roughness cannot be manufactured. On the other hand, if the gelatin is added above 100 ppm, an electrodeposited copper foil with low roughness may be obtained, but the characteristic of HTE(High Temperature Elongation, measured at 180° C.) which is one of the important characteristics of the copper foil can be deteriorated.

[0035] The amount of the addition of the HEC is minimum about 0.05 ppm through maximum about 50 ppm. Preferably, the amount range of the addition of the HEC is about 0.5~5 ppm. More preferably, the amount range of the same is about 1-3 ppm. In the case that the HEC is added with the

SPS and the gelatin in the electrolyte **600**, an electrodeposited copper foil with a lower roughness can be manufactured by an interaction of the additives.

[**0036**] If the HEC is added below 0.05 ppm in the electrolyte, a uniform electrodeposited copper foil may not be manufactured due to the decrease of the interaction. On the other hand, if the HEC is added above 50 ppm, protrusion may be extracted from the electrodeposited copper foil. In the case that copper clad laminates are produced by the electrodeposited copper foil with protrusion and then a PCB(Printed Circuit Board) is produced by the above copper clad laminates, the inferiority of the PCB is caused.

[**0037**] The amount of the addition of the SPS is minimum about 0.05 ppm through maximum about 20 ppm. Preferably, the amount range of the addition of the SPS is about 0.1~10 ppm. More peferably, the amount range of the same is about 0.5~3 ppm. The SPS is a material used as a brightener for an electrodepositing process. In the case that the SPS is added into the electrolyte **600**, it is possible to decrease the roughness of the electrodeposited copper foil in accordance with an interaction with the HEC and the gelatin.

[**0038**] If the SPS is added by below 0.05 ppm, the ability of the interaction is decreased, so that an electrodeposited copper foil **400** having ununiform roughness is manufactured. On the other hand, if the SPS is added by the amount of above 20 ppm, there is not a certain effect, but the cost is increased.

[**0039**] Three embodiments for manufacturing an electrodeposited copper foil **400** in such a manner that the amounts of the gelatin, HEC, and SPS added to the electrolyte **600** as an additive are different by the unit of ppm will be described in the following.

[**0040**] According to the embodiments of the present invention, the electrolysis condition is as follows. The electrolyte **600** basically consists of H_2SO_4 of about 100 g/l, Cu^{2+} of about 100 g/l, and Cl^- of below about 30 mg/l. The temperature of the electrolyte **600** is about 60° C., and the current density is about 100 A/dm^2.

[**0041**] The amounts of the additives added to the electrolyte **600** are shown in Table 1.

TABLE 1

	Gelatin	HEC	SPS
Embodiment 1	2.5 ppm	3 ppm	1.5 ppm
Embodiment 2	3.5 ppm	1 ppm	2.5 ppm
Embodiment 3	4.5 ppm	2 ppm	0.5 ppm

[**0042**] In the following, the comparison example 1 that HEC is not added as an additive and the comparison example 2 that Thiourea is newly added without adding HEC and SPS will be described. The comparison examples are performed for comparing the material properties of the electrodeposited copper foil **400** which is manufactured when the additives according to the present invention are all added with those of the electrodeposited copper foil which is manufactured when a certain additive among the additives according to the present invention is not added.

[**0043**] The electrolysis condition of the electrolyte of the comparisons except for the components of the additives is the same as the electrolysis condition of the electrolyte of the above embodiments of the present invention. The amounts of the additives added are shown in Table 2.

TABLE 2

	Gelatin	HEC	SPS	Thiourea
Comparison example 1	2.5 ppm	—	1.5 ppm	—
Comparison example 2	3.5 ppm	—	—	0.4 ppm

[**0044**] **FIG. 2** is a picture obtained by photographing an electrodeposited copper foil manufactured according to an embodiment **1** of the present invention using a SEM, and **FIG. 3** is a picture obtained by photographing an electrodeposited copper foil manufactured according to a comparison example 2 using a SEM. As shown therein, **FIGS. 2 and 3** illustrate the pictures of the SEM of the electrodeposited copper foil manufactured based on the embodiment 1 of the present invention and the electrodeposited copper foil manufactured based on the comparison example 2, respectively, before the post-treatments are performed.

[**0045**] As shown in **FIGS. 2 and 3**, it is known that the electrodeposited copper foil **400** manufactured based on the embodiment 1 of the present invention has a more smooth surface compared to the surface of the electrodeposited copper foil manufactured based on the comparison example 2. The above consequence represents that the roughness of the surface of the electrodeposited copper foil **400** manufactured based on the embodiment **1** of the present invention is relatively lower than that of the electrodeposited copper foil **400** manufactured based on the comparison example 2.

[**0046**] In Table 3, there are a roughness, tensile strength, elongation, high temperature tensile strength, and high temperature elongation of the electrodeposited copper foil manufactured based on each embodiment of the present invention and the electrodeposited copper foil manufactured based on each comparison example.

TABLE 3

	Roughness Rz(μm)	Tensile strength (kgf/mm^2)	Elongation (%)	High temperature tensile strength (kgf/mm^2)	High temperature elongation(%)
Embodiment 1	1.8	33.3	15.9	18.3	16.3
Embodiment 2	1.6	34.6	18.1	18.2	15.1
Embodiment 3	2.1	32.8	16.3	19.1	15.3
Comparison example 1	2.5	34.1	5.8	20.1	8.5
Comparison example 2	3.5	33.8	8.3	20.3	2.1

[**0047**] As shown in Table 3, it is known that the roughness of the electrodeposited copper foils manufactured according to the embodiments 1 through 3 are 1.61 μm through 2.1 pm, and the roughness of the electrodeposited copper foils manufactured according to the comparison examples 1 through 2 are about 2.5 pm through 3.5 μm. As a result, it is known that the electrodeposited copper foils manufactured according to the preferred embodiments of the present invention have a lower roughness, respectively, compared to the roughness of the electrodeposited copper foils manufactured according to the comparison examples.

[0048] The electrodeposited copper foil manufactured according to the present invention can be implemented with a conventional post-treatment for manufacturing the copper clad laminates which is used for printed circuit substrate.

[0049] As a conventional post-treatment of the electrodeposited copper foil **400**, there are a nodule process adapted to further form a nodule on one side or both sides of the electrodeposited copper foil for increasing an adhesion with a resin, a barrier process adapted to prevent a copper from being diffused into a resin layer, a corrosion resisting process adapted to prevent an oxidation of a copper foil, and a silane coupling agent process adapted to enhance a adhesion reliability when being adhered with a resin.

[0050] In addition, the electrodeposited copper foil **400** manufactured according to the present invention is formed of a copper clad laminate with an insulation film layer and an adhesive layer. The copper clad laminate is etched based on a circuit design and is adapted to manufacture a printed circuit substrate.

[0051] In the method for manufacturing a low roughness electrodeposited copper foil and an electrodeposited copper foil manufactured thereby, the amounts of additives cited in each embodiment are not limited thereto. In the present invention, various embodiments may be implemented in the addition ranges of the additives cited in the present invention. The electrodeposited copper foils **400** having various material properties may be adapted to the production of the copper clad laminate and the circuit substrate.

[0052] As the present invention may be embodied in several forms without departing from the spirit or essential characteristics thereof, it should also be understood that the above-described examples are not limited by any of the details of the foregoing description, unless otherwise specified, but rather should be construed broadly within its spirit and scope as defined in the appended claims, and therefore all changes and modifications that fall within the meets and bounds of the claims, or equivalences of such meets and bounds are therefore intended to be embraced by the appended claims.

We claim:

1. In a method for manufacturing an electrodeposited copper foil in which a rotating drum and an anode plate which is formed of a curve distanced from the outer surface of the drum by a certain distance are drowned in an electrolyte, said electrolyte consists of a sulfuric acid, copper ion and chloride ion, and the electrodeposited copper foil is deposited on the surface of the drum as a negative current is applied to the drum, and a positive current is applied to the anode plate, a method for manufacturing an electrodeposited copper foil which is characterized in that an additive which consists of a gelatin of 0.1~100 ppm, a HEC(Hydroxyethyl Cellulose) of 0.05 ppm~50 ppm, and a SPS(bis(sodiumsulfopropyl)disulfide) of 0.05~20 ppm is added to the electrolyte.

2. The method of claim 1, wherein the amount of the addition of the gelatin is 2~5 ppm.

3. The method of claim 1, wherein the amount of the addition of the HEC is 1~3 ppm.

4. The method of claim 1, wherein the amount of the addition of the SPS is 0.5~3 ppm.

5. The method of one among claims **1** through **4**, wherein a roughness of a matte side of the electrodeposited copper foil is larger than a roughness of a shiny side.

6. The method of one among claims **1** through **4**, further comprising a post-treatment process.

7. The method of claim 6, wherein said post-treatment process is formed of one or more than one selected from the steps of:

a nodule process for forming a nodule on one side or both sides of the electrodeposited copper foil for increasing an adhesion with a resin;

a barrier process for preventing a copper from being diffused into a resin layer;

a corrosion resisting process for preventing an oxidation of the electrodeposited copper foil; and

a silane coupling agent process for enhancing an adhesion reliability with the resin.

8. The method of either claim 1 or claim 2, wherein a molecular weight of the gelatin is above 10000.

9. The method of claim 1, wherein said electrolyte is formed of a sulfuric acid of 50~200 g/l, a copper ion of 30~150 g/l, and a chloride ion of 200 mg/l.

10. The method of claim 9, wherein a temperature of the electrolyte is 20~80° C.

11. The method of claim 9, wherein a current density of the electrolyte is 20~150 A/dm^2.

12. A low roughness electrodeposited copper foil manufactured by one method selected from the claims **1** through **4**.

13. The foil of claim 12, wherein a roughness of a matte side of the electrodeposited copper foil is larger than a roughness of a shiny side.

14. The foil of claim 12, further comprising a post-treatment process.

15. The foil of claim 14, wherein said post-treatment process is formed of one or more than one selected from the steps of:

a nodule process for forming a nodule on one side or both sides of the electrodeposited copper foil for increasing an adhesion with a resin;

a barrier process for preventing a copper from being diffused into a resin layer;

a corrosion resisting process for preventing an oxidation of the electrodeposited copper foil; and

a silane coupling agent process for enhancing an adhesion reliability with the resin.

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