

DESCRIPTION

COPPER FOIL INCLUDING RESISTIVE FILM LAYER

5

TECHNICAL FIELD

The present invention relates to a copper foil with a resistive film layer superior in film adhesiveness and having high peel strength.

10

BACKGROUND ART

Copper foil is generally used as a wiring material of a printed circuit board. This copper foil can be separated into an electrolytic copper foil and a rolled copper foil depending on the production method. The thickness of the copper foil can be
15 arbitrarily adjusted from an extremely thin copper foil having a thickness of $5\mu\text{m}$ to a thick copper foil having a thickness of roughly $140\mu\text{m}$.

These copper foils are bonded to a substrate formed from resin such as epoxy and polyamide, and are used as a printed circuit board. A copper foil is demanded to ensure sufficient adhesive strength with the resin to become the substrate. Thus, an
20 electrolytic copper foil uses a rough surface referred to as a matte surface that is generally formed during the production of the foil, and is used by additionally performing surface roughening treatment thereon. In addition, the rolled copper foil is also used by performing roughening treatment on its surface.

Recently, proposals have been made for additionally forming a thin film layer
25 formed from an electric resistive material on the copper foil as the wiring material (refer to Patent Documents 1 and 2). An electric resistive element is indispensable in an electronic circuit board, but if a copper foil comprising a resistive layer is used, the electric resistive film layer formed on the copper foil merely needs to be etched with an etching solution such as copper chloride in order to expose the resistive element.

30 Accordingly, as a result of building the resistor in the substrate, the limited substrate surface area can be effectively used in comparison to conventional methods that were limited to mounting a chip resistive element on the substrate surface using the solder bonding method.

In addition, design restrictions will decrease as a result of forming a resistive

element in a multilayer substrate, and improvement in the electrical characteristics can be sought by shortening the circuit length. Thus, if a copper foil comprising a resistive layer is used, solder bonding will become unnecessary or considerably reduced, and weight reduction and improvement in reliability can be sought. As described above, a substrate with a built-in electric resistive film possesses numerous advantages.

The copper foil to become the base for use in the resistive material is subject to surface treatment on the precondition that a resistive layer is to be additionally formed thereon, and, although it is ordinarily different from those used for a standard printed circuit board wiring, it is the same in that the adhesive strength with the resin is ensured through roughening.

When evaluating the adhesive strength of the resistive material, it is necessary to examine both the strength between the copper foil and the resistive film and the strength between the resistive film and the resin, and in the tensile test or the like, peeling occurs from the weaker boundary face. In either case, it is known that larger the surface roughness, higher the adhesive strength. The adhesive strength is considered to be affected by the surface roughness and other factors such as the surface chemical species (element species).

Meanwhile, demands for inhibiting the surface roughness of the resistive material are increasing due to demands for the formation of even smaller resistance circuits and improvement in high frequency characteristics which are being sought in printed circuit boards that continue to become more sophisticated. In order to realize the above, improvement in the adhesive strength without depending on the surface roughness is essential.

[Patent Document 1] Japanese Patent No.3311338

[Patent Document 2] Japanese Patent No.3452557

DISCLOSURE OF THE INVENTION

Thus, an object of the present invention is to provide a copper foil with a resistive film layer enabling the resistor to be built into the substrate as well as improving the adhesiveness thereof by additionally forming an electric resistive film layer on the copper foil.

As a result of intense study to achieve the foregoing object, the present inventors discovered that it is effective to form a layer for increasing the adhesive strength between the copper foil and the electric resistive film layer.

Based on the foregoing discovery, the present invention provides:

- 5 1) A copper foil comprising an electric resistive film layer, wherein a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000 $\mu\text{g}/\text{dm}^2$ is formed on a roughened or a gloss surface of a copper foil, a stabilization layer having a thickness of 5Å to 100Å formed from at least one component selected from zinc oxide, chromic oxide, and nickel oxide is formed on the copper-zinc alloy layer, and a film layer
10 formed from an electric resistive material is formed on the stabilization layer.

When using a copper foil comprising an electric resistive film layer as a film for use in a circuit board, if a stabilization layer formed from at least one component selected from zinc oxide, chromic oxide, and nickel oxide is formed on the copper foil and an electric resistive layer is additionally formed thereon, it was considered that
15 sufficient adhesive strength with the copper foil could be obtained. However, there was a problem in that the adhesive strength was insufficient when using a copper foil having small roughness in which the roughening level of the base copper foil was lowered.

In order to overcome the foregoing problem, the present inventors discovered
20 that it is effective to form a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000 $\mu\text{g}/\text{dm}^2$ prior to forming the foregoing stabilization layer. Improvement in the adhesive strength between the copper foil and the copper-zinc alloy layer and stabilization layer, and with the electric resistive film layer can be evaluated based on the peel strength.

25 As needed, a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000 $\mu\text{g}/\text{dm}^2$ is formed on the face of the copper foil that was subject to this kind of surface treatment. This is an important process for improving the adhesive strength. With a copper-zinc alloy layer in which the zinc content per unit area is less than 1000 $\mu\text{g}/\text{dm}^2$, the adhesive strength will not improve. Moreover, with a
30 copper-zinc alloy layer in which the zinc content per unit area exceeds 9000 $\mu\text{g}/\text{dm}^2$, this is not preferable since the chemical resistance (corrosion due to etching solution) will be inferior. This is because the inclusion of a large amount of zinc will cause the problem of deteriorating the corrosion resistance.

This copper-zinc alloy layer can be formed by way of electrodeposition. The

zinc content in the copper-zinc alloy for the electrodeposition is arbitrary. In other words, this includes a layer in which zinc is diffused to the copper foil after the electrodeposition. It will suffice so long as it becomes a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000 $\mu\text{g}/\text{dm}^2$. Consequently, the thickness of the copper-zinc alloy layer corresponds to a range of roughly 100 to 1200Å.

A stabilization layer having a thickness of 5Å to 100Å formed from at least one component selected from zinc oxide, chromic oxide, and nickel oxide is formed on the copper-zinc alloy layer that was formed as described above.

This stabilization layer has a limited effect as described above, but it also yields an effect of improving the adhesiveness with the copper foil.

Zinc oxide, chromic oxide, and nickel oxide are all effective as the stabilization layer and these may also be used in combination. The stabilization layer prevents the oxidation corrosion of the copper foil, prevents the decomposition of the dielectric base material caused by the copper, and possesses the function of maintaining stable peel strength. The thickness is normally set from 5Å to 100Å, but may be set to 100Å or more as needed; that is, the thickness may be set from 200 to 300Å. However, if the thickness is less than 5Å, the function of the stabilization layer cannot be achieved and the adhesive strength will decrease, which is not desirable.

An electric resistive film layer is formed on the stabilization layer that was formed as described above. The electric resistive film layer is arbitrarily decided according to the circuit design. In other words, the selection of the type of electric resistive material and the film thickness is decided in consideration of the function of the resistive element, and there is no particular limitation.

As an example to be used as a material of the electric resistive element, materials such as vanadium, tungsten, zirconium, molybdenum, tantalum, nickel, and chromium may be used. Metal with a relatively high electrical resistance is used; it can be used as an independent film or as an alloy film with other elements.

In addition, even with materials with a relatively low electrical resistance such as aluminum, silicon, copper, iron, indium, zinc, and tin, these can obviously be used if the electrical resistance increases as a result of being alloyed with other elements.

For instance, these would be materials such as NiCr alloy and NiCrAlSi in which the electric resistive element is attracting attention. Moreover, the oxides, nitrides and silicides of materials selected from a group of the oxides, nitrides and

silicides of the foregoing elements may also be used. As described above, the selection of these materials is made arbitrarily according to the circuit design, and it should be understood that the present invention is not limited to these materials.

Upon forming this electric resistive film layer, a physical surface treatment method such as a sputtering method, a vacuum deposition method or an ion beam plating method, a chemical surface treatment method such as a thermal decomposition method or a gas-phase reaction method, or a wet surface treatment method such as an electrodeposition method or an electroless deposition method may be used.

Generally speaking, the electrodeposition method has an advantage in that it can be performed at low cost. In addition, since the sputtering method is able to obtain a film having a uniform thickness and isotropic nature, it has an advantage in that it is able to obtain a high-quality resistive element.

The formation of this electric resistive film layer is made in accordance with the usage of the film, and the deposition method or plating method should be suitably selected in accordance with the nature of that electric resistive film layer.

2) With the copper foil comprising an electric resistive film layer of the present invention, the foil thickness of the copper foil may be 5 to 70 μ m, preferably 5 to 35 μ m. The thickness of the copper foil may be arbitrarily selected in accordance with the usage, but production within the foregoing range is efficient since there are certain restrictions based on the manufacturing conditions.

3) The present invention additionally provides a copper foil comprising an electric resistive film layer wherein an electric resistive layer is formed on a matte surface (rough surface) of an electrolytic copper foil or a face of a rolled copper foil subject to roughening treatment.

It is also possible to further perform roughening treatment of adhering knotty particles on the matte surface of the electrolytic copper foil. Moreover, as needed, it is also possible to perform roughening treatment to the rolled copper foil. In the foregoing roughening treatment, it is possible to obtain a roughened surface of a low profile copper foil or a standard profile of Rz 0.3 to 10.0 μ m.

As a result of using the copper foil with the electric resistive film layer of the present invention built therein, an effect is yielded in that the solder bonding will become unnecessary or be considerably reduced and the mounting process will be significantly simplified as a result of merely having to etch the electric resistive film

layer formed on the copper foil using an etching solution such as copper chloride and exposing the resistive element without having to newly form an independent electric resistive element upon designing the circuit.

In addition, there are advantages in that the space can be expanded and miniaturization and weight reduction can be achieved since the components to be mounted and the soldering process can be reduced. Consequently, it is possible to improve the freedom of the circuit design. Moreover, as a result of the resistor being built into the copper foil as described above, the effect of improving the signal characteristics in a high frequency range is yielded.

The present invention also yields a superior effect of being able to overcome the deterioration of the adhesive strength, which is a defect encountered in copper foils with a built-in electric resistive film layer, and comprising favorable heat resistance and acid resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing the outline of an electrolytic copper foil production system; and

Fig. 2 is a diagram showing the outline of a surface treatment system.

BEST MODE FOR CARRYING OUT THE INVENTION

Fig. 1 shows the outline of the production system of the electrolytic copper foil. With this system, a cathode drum is placed in an electrolysis tank housing an electrolytic solution. The cathode drum 1 is able to rotate in a state of being partially (roughly the lower half) being immersed in the electrolytic solution.

An insoluble anode (positive electrode) 2 is provided so as to encompass the peripheral lower half of the cathode drum 1. There is a fixed gap 3 between the cathode drum 1 and the anode 2, and the electrolytic solution is caused to flow therebetween. Two anode plates are arranged in the system of Fig. 1.

In Fig. 1, the electrolytic solution is supplied from the bottom, and the electrolytic solution passes through the gap 3 between the cathode drum 1 and the anode 2, overflows from the upper edge of the anode 2, and this electrolytic solution is configured to additionally circulate. A prescribed voltage can be maintained between

the cathode drum 1 and the anode 2 via a rectifier.

As the cathode drum 1 rotates, the thickness of the copper that electrodeposited from the electrolytic solution increases, and the raw foil 4 is peeled and continuously rolled up when it becomes a certain thickness. With the raw foil
5 produced as described above, the thickness is adjusted by the distance between the cathode drum 1 and the anode 2, the flow velocity of the supplied electrolytic solution, or the supplied electrical quantity.

The copper foil produced with the foregoing copper foil production system will have a mirror surface (gloss surface) as the face that comes in contact with the
10 cathode drum, and the face on the other side will become a rough surface (matte surface). The thickness of the electrolytic copper foil can be arbitrarily selected. Normally, a copper foil having thickness of $9\mu\text{m}$ to $35\mu\text{m}$ can be used.

The copper foil produced as described above is subsequently subject to the cleaning process of removing the oxide film on the surface, and further subject to a
15 water washing process. In the cleaning process, normally a sulfuric acid aqueous solution of 10 to 80g/L is used.

In the foregoing description, although the production of the electrolytic copper foil was explained, with respect to the rolled copper foil, the melted and cast ingot can be subject to annealing and hot rolling, and additionally subject to cold rolling in order
20 to product a copper foil having the necessary thickness. Since all rolled copper foils have a gloss surface, roughening treatment is performed as needed. For the roughening treatment, publicly known roughening treatment methods may be used.

An example of the roughening treatment is shown below. In addition, the roughening treatment can also be applied to the gloss surface and matte surface
25 (rough surface) of the electrolytic copper foil.

Cu ion concentration: 10 to 30g/L

Sulfuric acid concentration: 20 to 100g/L

Electrolytic solution temperature: 20 to 60°C

Current density: 5 to 80A/dm^2

30 Treatment time: 0.5 to 30 seconds

Zinc-copper alloy plating treatment is performed to the electrolytic copper foil or rolled copper foil produced as described above. The zinc-copper alloy plating treatment bath composition and electrodeposition conditions are as follows.

(Zinc-copper Alloy Plating Bath Composition and Treatment Conditions)

Bath Composition:

CuCN: 60 to 120g/L

Zn (CN)₂: 1 to 10g/L

NaOH: 40 to 100g/L

5 Na (CN): 10 to 30g/L

pH: 10 to 13

Bath temperature: 60 to 80°C

Current density: 100 to 10000A/dm²

Treatment time: 2 to 60 seconds

10 It is thereby possible to form a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000μg/dm². The foregoing electrodeposition shows the favorable zinc-copper alloy plating conditions. So long as it is possible to form a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000μg/dm², there is no particular limitation to the foregoing conditions.

15 Thus, it is also possible to plate the copper with zinc and perform thermal diffusion to form a copper-zinc alloy layer. Moreover, since heat will generally arise in the press process, if zinc plating is formed, the copper-zinc alloy layer will be formed based on thermal diffusion, and this may also be used. A favorable zinc plating example is shown below.

20 (Zinc Plating Bath Composition and Plating Conditions)

Bath Composition:

ZnSO₄·7H₂O: 50 to 350g/L

pH: 2.5 to 4.5

Bath temperature: 40 to 60°C

25 Current density: 5 to 40A/m²

Treatment time: 1 to 30 seconds

Subsequently, a stabilization layer having a thickness of 5Å to 100Å formed from at least one component selected from zinc oxide, chromic oxide, and nickel oxide is formed on the zinc-copper alloy layer.

30 As one illustrative embodiment, a coating layer may be formed using an electrolytic solution containing zinc ions and chromium ions. For the zinc ion source in the electrolytic solution, ZnSO₄, ZnCO₃, ZnCrO₄ and the like may be used. As the chromium ion source in the electrolytic solution, salt or compound of hexahydric chromium such as ZnCrO₄ and CrO₃ may be used.

The zinc ion concentration in the electrolytic solution is set from 0.1 to 2g/L, preferably 0.3 to 0.6g/L, and more preferably 0.4 to 0.5g/L. Moreover, the chromium ion concentration in the electrolytic solution is set from 0.3 to 5g/L, preferably 0.5 to approximately 3g/L, and more preferably 0.5 to 1.0g/L. Incidentally, these conditions
5 are merely conditions for performing plating efficiently, and conditions outside the foregoing range may also be used as needed.

As another illustrative embodiment, nickel oxide and nickel metal, or zinc oxide or chromic oxide or the combination thereof may be coated in order to form the foregoing stabilization layer. As the nickel ion source of the electrolytic solution,
10 Ni_2SO_4 and NiCO_3 may be independently or jointly used.

The nickel ion concentration in the electrolytic solution is preferably 0.2g/L to 1.2g/L. It is also possible to use a stabilization layer containing phosphorus as described in U.S. Patent No.5,908,544. Incidentally, these are conditions for efficiently forming a stabilization layer having a thickness of 5Å to 100Å formed from at
15 least one component selected from zinc oxide, chromic oxide, and nickel oxide, and conditions outside the foregoing range may also be used as needed.

The electrolytic solution may also contain other conventional additives such as Na_2SO_4 in a concentration of 1 to 50g/L, preferably 10 to 20g/L, and more preferably 12 to 18g/L. The electrolytic solution pH is generally set from 3 to 6,
20 preferably 4 to 5, and more preferably 4.8 to 5.0.

The electrolytic solution temperature is set from 20°C to 100°C, preferably 25°C to 45°C, and more preferably 26°C to 44°C.

As shown in Fig. 2, an anode 48 is arranged adjacent to each side of the copper foil 12 in order to provide current density to the copper foil 12. The guide
25 roller 46 is a cathode roller, and, when voltage is applied to the anode 48 from the power source (not shown), for instance, the stabilization layer 49 formed from zinc oxide and chromic oxide is deposited on the gloss side 14 exposed on the copper foil 12 and the matte surface 16. Fig. 3 is a cross section showing the copper foil 12 having the stabilization layer 49 on the gloss side 14 and the non-gloss side 16.

The current density is set from 1 to 100A/ft² (10.8 to 1080A/m² approximately), preferably 25 to 50A/ft² (270 to 540A/m² approximately), and more preferably 30A/ft² (approximately 320A/m²). When providing a plurality of anodes, the current density
30 may be changed between the anodes.

The plating time is set from 1 to 30 seconds, preferably 5 to 20 seconds, and

more preferably approximately 15 seconds. In a certain illustrative embodiment, the total treatment time is 3 to 10 seconds approximately on the gloss side or on the smooth side, and 1 to 5 seconds approximately on the non-gloss side.

Moreover, as a preferable example, the molar ratio of the chromium ions in relation to the zinc ions in the electrolytic solution is 0.2 to 10, preferably 1 to 5, and more preferably approximately 1.4. According to the present invention, the thickness of the stabilization layer applied to the copper foil is preferably 5Å to 100Å, more preferably 20Å to 50Å.

In the illustrative embodiment explained above, although the stabilization layer is configured from chromic oxide and zinc oxide, the stabilization layer may also be configured from only chromic oxide.

The preferable bath conditions for applying the chromic oxide stabilization layer are as follows.

1 to 10g/L Cr O₃ solution

Preferably 5g/L Cr O₃

pH-2

Bath temperature: 25°C

5 to 10 seconds and 10 to 30A/ft² (108 to 320A/m²)

Immersion treatment: 10 seconds

Cleaning is performed after the process of forming the stabilization layer. In the cleaning process, for instance, water is sprayed on the face of the copper foil (including a stabilization layer) with a spray device set above and below the copper foil, and the residual electrolytic solution thereon is removed by rinsing and cleaning. The container set below the spray nozzle can be used to collect the cleaned solution.

A copper foil having a stabilization layer on the upper surface thereof is further dried. As shown in the illustrative embodiment, the mandatory air oven is set above and below the copper foil, and air is discharged therefrom to dry the copper foil surface.

A layer formed from an electric resistive material is additionally formed on the copper foil to which the stabilization layer has been formed. As an example of the electric resistive layer, an electric resistive element such as NiCr alloy and NiCrAlSi alloy can be used. The layer formed from the electric resistive material is demanded based on the circuit board design, and can be arbitrarily selected. Accordingly, it is not necessary to limit this to a specific material.

To improve the adhesiveness with the base material (base sheet), various types of silane treatment may also be performed on the resistive layer as needed. But, this silane treatment is arbitrary, and the present invention is not limited thereto.

[Examples]

The present invention is now explained in detail with reference to the Examples. These Examples are merely illustrative, and the present invention shall in no way be limited thereby. In other words, various modifications and other embodiments based on the technical spirit claimed in the claims shall be included in the present invention as a matter of course.

(Example 1)

In the following Examples, an electrodeposited copper foil having a thickness of $18\mu\text{m}$ was used. A copper-zinc alloy layer was formed on the side of the rough surface (matte surface) of the electrolytic copper foil.

The copper-zinc alloy layer was formed with the following treatment conditions in which the zinc content per unit area is approximately $3500\mu\text{g}/\text{dm}^2$ (last two digits were rounded off). The coating amount was adjusted with the treatment time.

(Copper-zinc Alloy Plating Bath Composition and Plating Conditions)

Bath Composition:

CuCN: 90g/L

Zn (CN)₂: 5g/L

NaOH: 70g/L

Na (CN): 20g/L

Bath temperature: 70°C

Current density: $500\text{A}/\text{dm}^2$

Treatment time: 5 to 20 seconds

Subsequently, a stabilization layer of approximately $50\text{\AA}$ formed from zinc oxide-chromic oxide was formed on the copper-zinc alloy layer under the following treatment conditions.

(Stabilization Treatment Bath Composition and Treatment Conditions)

Bath Composition:

0.53g/L of zinc as ZnSO_4

0.6g/L of chromium as CrO_3

Na_2SO_4 11g/L

Bath pH: 5.0

Bath temperature: 42°C

Current density: 85 to 160A/m²

Plating time: 3 to 4 seconds

5 Subsequently, an alloy electric resistive material of 80% nickel (Ni) and 20% chromium (Cr) was deposited on the foregoing stabilization layer under the following conditions.

Ni/Cr alloy sputtering:

14-inch sputtering device

10 Power: 5 to 8kw

Linear velocity: 1.4 to 2.2ft/min (0.43 to 0.67m/min)

Ni/Cr alloy thickness: approximately 100Å

Incidentally, the sheet resistivity of this resistive material was approximately 160Ω/square.

15 The normal peel value, peel value after solder treatment (heat resistance), and peel value after hydrochloric acid treatment (resistance to hydrochloric acid) regarding the coating layer to the copper foil were checked.

Incidentally, the peel value after the solder treatment was obtained by measuring the peel value after immersion (that is, in a state of being subject to heat treatment) in a 260°C molten solder bath for 20 seconds; that is, the peel value after the solder treatment shows the peel value after this treatment (after receiving the thermal effect). This is used for evaluating the heat resistance.

20 In addition, the peel value after the hydrochloric acid treatment shows the peel value after immersion in 18wt% hydrochloric acid at room temperature for 1 hour. In other words, this is used for evaluating the resistance to hydrochloric acid. This is hereafter the same.

25 Consequently, the normal peel value was 0.81kg/cm, the peel value after the solder treatment (heat resistance) was 0.77kg/cm, and the peel value after the hydrochloric acid treatment (resistance to hydrochloric acid) was 0.70kg/cm, and 30 there was no deterioration after the solder treatment and after the hydrochloric acid treatment, and all cases showed favorable characteristics.

[Table 1]

	Zinc Content of Copper-Zinc Alloy Layer ($\mu\text{g}/\text{dm}^2$)	Normal Peel Strength (kg/cm)	After Immersion in Solder Bath (kg/cm)	After Immersion in Hydrochloric Acid (kg/cm)
Example 1	3500	0.81	0.77	0.70
Example 2	2000	0.71	0.60	0.63
Example 3	2500	0.76	0.73	0.67
Example 4	3000	0.81	0.75	0.70
Example 5	4000	0.84	0.80	0.70
Example 6	4500	0.86	0.82	0.73
Example 7	5000	0.88	0.86	0.71
Example 8	5500	0.92	0.90	0.69
Example 9	6000	0.91	0.87	0.63
Example 10	6500	0.90	0.87	0.56
Example 11	7000	0.95	0.90	0.55
Comparative Example 1	500	0.49	0.49	0.45
Comparative Example 2	10000	0.93	0.91	0.44

The numerical value of the last two digits of the zinc content has been rounded off.

After Immersion in Solder Bath: Shows the peel strength after immersion in 260°C molten solder bath.

After Immersion in Hydrochloric Acid: Shows the peel strength after immersion in 18wt% hydrochloric acid.

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(Example 2-11) [Zinc Content]

Subsequently, based on the conditions of Example 1 that showed favorable characteristics, copper-zinc alloy layers were formed by changing the zinc content per unit area (1000 to 9000 $\mu\text{g}/\text{dm}^2$). Similarly the last two digits were rounded off. The treatment conditions other than the zinc content of the copper-zinc alloy layer were the same as Example 1. The coating amount was adjusted based on the treatment time. The results are shown in Table 1.

Incidentally, as comparisons, copper-zinc alloy layers having a zinc content outside the conditions of the present invention are shown as Comparative Example 1 and Comparative Example 2.

As evident from Table 1, when the zinc content in the copper-zinc alloy layer is approximately 3500 $\mu\text{g}/\text{dm}^2$ (last two digits were rounded off) (Example 1), the normal peel strength, heat resistance, and resistance to hydrochloric acid were favorable and showed well-balanced characteristics.

Meanwhile, as the zinc content per unit area increased, although the normal peel strength and heat resistance increased, the resistance to hydrochloric acid contrarily tended to decrease. Contrarily, as the zinc content per unit area decreased, although the resistance to hydrochloric acid increased, the normal peel strength and heat resistance tended to decrease.

Comparative Example 1 showed low normal peel strength, low heat resistance, and low resistance to hydrochloric acid since the zinc content was low, and Comparative Example 2 showed high normal peel strength and heat resistance but the resistance to hydrochloric acid was inferior because the zinc content was excessive, and both cases exceeded the tolerable limit and were not suitable for practical application. Thus, the existence of a copper-zinc alloy layer is extremely effective in improving the normal peel strength, heat resistance, and resistance to hydrochloric acid.

(Example 1 to Example 1-4) [Copper Foil Thickness]

Subsequently, based on the conditions of Example 1 that showed favorable characteristics, the normal peel strength, heat resistance, and resistance to hydrochloric acid in cases of changing the thickness of the copper foil were checked. Conditions other than changing the thickness of the copper foil were the same as Example 1. The coating amount was adjusted based on the treatment time. The results are shown in Table 2.

In the case of Example 1, although the electrolytic copper foil having a thickness of $18\mu\text{m}$ was used, the normal peel changed considerably according to the foil thickness when the thickness was changed within the range of $9\mu\text{m}$ to $35\mu\text{m}$. In other words, the peel strength increased according to the increase in the copper foil thickness.

Nevertheless, the deterioration rate of the peel value after the solder treatment and the peel deterioration rate after hydrochloric acid treatment did not change significantly. Thus, it was discovered that the peel strength after the solder treatment and the peel strength after the hydrochloric acid treatment are not affected largely by the copper foil thickness in terms of the deterioration rate after treatment. The results are shown in Table 2. Generally, it could be said that the peel strength increases pursuant to the increase in the copper foil thickness.

[Table 2]

	Copper Foil Thickness (μm)	Normal Peel Strength (kg/cm)	Peel Strength After Immersion in Solder Bath (kg/cm)	Deterioration Rate After Immersion in Solder Bath (%)	Peel Strength After Immersion in Hydrochloric Acid (kg/cm)	Deterioration Rate After Immersion in Hydrochloric Acid (%)
Example 1	18	0.81	0.77	4.9	0.70	13.6
Example 1-2	9	0.59	0.57	3.4	0.50	15.3
Example 1-3	12	0.72	0.70	2.8	0.57	18.1
Example 1-4	35	1.24	1.19	4.0	1.02	17.7

The zinc content was $3500\mu\text{g}/\text{dm}^2$ in all cases.

Deterioration Rate: $(\text{Pre-treatment peel strength} - \text{Post-treatment peel strength}) / \text{Pre-treatment peel strength} \times 100(\%)$

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(Example 12) [Silane Treatment]

In this Example, electrodeposited copper foils having a thickness of $18\mu\text{m}$ and $35\mu\text{m}$ were used, and the rough surface of the electrolytic copper foil was used as is, and a copper-zinc alloy plated layer formed on the surface subject to the roughening treatment under the same conditions as Example 1; that is, under the same plating conditions as Example 1 using the copper-zinc alloy plating bath.

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The foregoing roughening treatment conditions are as follows:

Cu ion concentration: 20g/L

Sulfuric acid concentration: 60g/L

15

Electrolytic solution temperature: 40°C

Current density: $30\text{A}/\text{dm}^2$

Treatment time: 5 seconds

Based on the above, a copper-zinc alloy layer in which the zinc content per unit area is approximately $3500\text{mg}/\text{m}^2$ (last two digits were rounded off) was formed.

20

Subsequently, a Cr-Zn oxide stabilization layer was formed on this copper-zinc alloy layer as with Example 1.

Further, an alloy electric resistive material of 80% nickel (Ni) and 20% chromium (Cr) was formed on this Cr-Zn oxide stabilization layer via sputtering. These conditions were also the same as Example 1.

25

Subsequently, silane treatment (TEOS: Tetraethoxysilane) was performed on the resistive layer. The results are shown in Table 3. As shown in Table 3, it can be understood that the normal peel strength increased and, therefore, the silane treatment is effective.

[Table 3]

	Copper Foil Thickness (μm)	Roughening Treatment	Silane Treatment	Normal Peel Strength (kg/cm)
Example 12	18	No	Yes	1.00
Example 12-2	35	No	Yes	1.50
Example 12-3	18	Yes	Yes	1.30
Example 12-4	35	Yes	Yes	1.60

The zinc content was $3500\mu\text{g}/\text{dm}^2$ in all cases.
Silane treatment (TEOS) was performed on the resistive layer.

5 (Example 13) [Cr Resistive Film]

Under the conditions of Example 1, a copper-zinc alloy layer in which the zinc content per unit area is approximately $3500\mu\text{g}/\text{dm}^2$ (last two digits were rounded off) was formed, and a Cr-Zn oxide stabilization layer was formed on this Cu-Zn alloy layer.

10 Subsequently, a chromium resistive film was formed on this Cr-Zn oxide stabilization layer via sputtering.

The chromium sputtering conditions were as follows.

A 14-inch sputtering device was used.

Power: 5 to 8kw

15 Linear velocity: 1.8 to 2.8ft/min (0.55 to 0.85m/min)

Chromium thickness: Six types; $100\text{\AA}$, $1000\text{\AA}$, $1200\text{\AA}$, $2000\text{\AA}$, $3000\text{\AA}$, and $4000\text{\AA}$

20 The normal peel strength, heat resistance, resistance to hydrochloric acid of Example 13 were checked, and, although not shown in the tables, they all showed favorable characteristics as with Example 1. Accordingly, it can be understood that the formation of a copper-zinc alloy layer is effective regardless of the type and thickness of the resistive layer.

(Example 14 to Example 14-4) [Ni/Cr/Al/Si Alloy Resistive Film]

25 Under the conditions of Example 1, a copper-zinc alloy layer in which the zinc content per unit area is approximately $3500\mu\text{g}/\text{dm}^2$ (last two digits were rounded off) was formed, and a chromium-zinc oxide stabilization layer was formed on this copper-zinc alloy layer.

30 Subsequently, an alloy of 56% nickel (Ni), 38% chromium (Cr) and as dopants 4% aluminum (Al) and 2% silicon (Si) were deposited on this chromium-zinc oxide stabilization layer under the following conditions.

Ni/Cr/Al/Si alloy sputtering:

14-inch sputtering device

Power: 0.85 to 2.3kw

Linear velocity: 0.49ft/min (0.15m/min)

5 Sheet resistivity: approximately 90 to 300 Ω /square

Films having the sheet resistance shown in Table 4 were formed as Example 14 to Example 14-4. The normal peel strength, heat resistance, and resistance to hydrochloric acid were checked, and, as shown in Table 4, they all showed favorable characteristics as with Example 1. Accordingly, it can be understood that the formation of a copper-zinc alloy layer is effective regardless of the Ni/Cr/Al/Si alloy resistive layer.

[Table 4]

(Example 14) [Ni/Cr/Al/Si Alloy Resistive Film]

	Sheet Resistance (ohm/sq)	Normal Peel Strength (kg/cm)	Peel Strength After Immersion in Solder Bath (kg/cm)	Peel Strength After Immersion in Hydrochloric Acid (kg/cm)
Example 14	94	0.81	0.75	0.72
Example 14-2	135	0.79	0.77	0.70
Example 14-3	233	0.82	0.78	0.71
Example 14-4	286	0.80	0.74	0.73

15 The zinc content was 3500 μ g/dm² in all cases.
The thickness of the copper foil was 18 μ m in all cases.

(Example 15 to Example 15-4) [Rolled Copper Foil]

20 In these Examples, rolled copper foils of 9 μ m, 12 μ m, 18 μ m, and 35 μ m were used. These rolled copper foils were subject to roughening treatment under the following conditions.

Cu ion concentration: 20g/L

Sulfuric acid concentration: 60g/L

Electrolytic solution temperature: 40°C

Current density: 30A/dm²

25 Treatment time: 5 seconds

Subsequently, a Zn plated layer of 3500 μ g/dm² was formed on the rolled copper foils subject to the roughening treatment under the following conditions. The thickness of the zinc plating was adjusted based on the treatment time.

Zinc Plating Bath Composition:

30 ZnSO₄·7H₂O: 50 to 350g/L

pH: 3

Bath temperature: 50°C

Current density: 20A/m²

Treatment time: 2 to 3 seconds

5 The copper foil to which the treatment layer was formed was subject to heat treatment at 300°C to form a copper-zinc alloy layer. The zinc content per unit area of the copper-zinc alloy layer formed as described above was approximately 3500μg/dm² (last two digits were rounded off).

10 Subsequently, a zinc oxide-chromic oxide stabilization layer of approximately 50Å was formed on the copper-zinc alloy layer under the following treatment conditions.

Stabilization treatment:

0.53g/L of zinc as ZnSO₄

0.6g/L of chromium as CrO₃

15 Na₂SO₄ 11g/L

Bath pH: 5.0

Bath temperature: 42°C

Current density: 85 to 160A/m²

Plating time: 3 to 4 seconds

20 Subsequently, an alloy electric resistive material of 80% nickel (Ni) and 20% chromium (Cr) was deposited on the foregoing stabilization layer under the following conditions.

Ni/Cr alloy sputtering:

14-inch sputtering device

25 Power: 5 to 8kw

Linear velocity: 1.4 to 2.2ft/min (0.43 to 0.67m/min)

Ni/Cr alloy thickness: approximately 100Å

Incidentally, the sheet resistivity of this resistive material was approximately 160Ω/square.

30 The normal peel strength, heat resistance (peel strength after solder treatment), resistance to hydrochloric acid (peel strength after hydrochloric acid treatment) regarding the coating layer on the copper foil were checked. The results are shown in Table 5. As shown in Table 5, the normal peel strength was 0.64 to 1.22kg/cm, the peel strength after solder immersion was 0.60 to 1.16kg/cm, and the

peel strength after 18wt% hydrochloric acid immersion was 0.53 to 1.09kg/cm, and they all showed favorable characteristics.

Moreover, the results were the same, when testing was performed by changing the thickness of the Cu-Zn alloy layer as with Example 2-11. Accordingly, it can be understood that the formation of a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000 $\mu\text{g}/\text{dm}^2$ in both the electrolytic copper foil and the rolled copper foil is effective in improving the adhesive strength (increase of normal peel strength), heat resistance and acid resistance.

[Table 5]

	Copper Foil Thickness (μm)	Normal Peel Strength (kg/cm)	After Immersion in Solder Bath (kg/cm)	After Immersion in Hydrochloric Acid (kg/cm)
Example 15	9	0.64	0.60	0.53
Example 15-2	12	0.72	0.69	0.59
Example 15-3	18	0.89	0.85	0.69
Example 15-4	35	1.22	1.16	1.09

The zinc content was 3500 $\mu\text{g}/\text{dm}^2$ in all cases.

INDUSTRIAL APPLICABILITY

As a result of using the copper foil with the electric resistive film layer of the present invention built therein, an effect is yielded in that the solder bonding will become unnecessary or be considerably reduced and the mounting process will be significantly simplified as a result of merely having to etch the electric resistive film layer formed on the copper foil using an etching solution such as copper chloride and exposing the resistive element without having to newly form an independent electric resistive element upon designing the circuit. In addition, as a result of considerably reducing the circuit design and production process and the resistor being built into the copper foil as described above, the effect of improving the signal characteristics in a high frequency range is yielded. The present invention also yields a superior effect of being able to overcome the deterioration of the adhesive strength, which is a defect encountered in copper foils with a built-in electric resistive film layer, and comprising favorable heat resistance and acid resistance. Thus, the present invention is useful as a printed circuit board.

CLAIMS

1. A copper foil comprising an electric resistive film layer, wherein a copper-zinc alloy layer in which the zinc content per unit area is 1000 to 9000 $\mu\text{g}/\text{dm}^2$ is formed on
5 a roughened surface or a gloss surface of a copper foil, a stabilization layer having a thickness of 5 $\text{\AA}$ to 100 $\text{\AA}$ formed from at least one component selected from zinc oxide, chromic oxide, and nickel oxide is formed on the copper-zinc alloy layer, and a film layer formed from an electric resistive material is formed on the stabilization layer.
2. The copper foil comprising an electric resistive film layer according to claim 1,
10 wherein the foil thickness of the copper foil is 5 to 35 μm .
3. The copper foil comprising an electric resistive film layer according to claim 1 or claim 2, wherein an electric resistive layer is formed on a matte surface of an electrolytic copper foil or a face of a rolled copper foil subject to roughening treatment.