

SPECIFICATION

Production of strippable copper layer on aluminium carrier and composite structure so obtained

The present invention is concerned with a composite structure comprising a carrier layer of aluminium having on a surface thereof a covering layer of copper, the aluminium layer being readily removable by mechanical means from the copper layer, and with a process for producing such a composite structure.

Composite structures of this kind are used, in particular, in the printed circuit industry. In this use, the copper layer of the composite structure is bonded to an insulating substrate by a suitable laminating technique, the aluminium carrier layer is mechanically separated from the copper layer which has been bonded to the insulating substrate, and the desired circuit pattern is then formed in the copper layer.

While this technique is used extensively today in thin foil applications, it is not devoid of problems. For example, difficulties are often experienced with the laminating procedure. To obtain good electrical, mechanical and chemical properties in the final product, it is often necessary to use high temperatures (often in excess of 400°F (204°C)) and pressures. While these conditions give a good bond between the copper foil and the insulating substrate, they unfortunately reduce the strippability of the aluminium carrier layer. Obviously, this problem of reduced strippability is to be avoided, if possible.

We have now developed a process for producing such composite structures which gives structures which are suitable for high temperature laminating and in which the carrier layer of aluminium can be readily separated from the copper layer by simple mechanical means after the laminating procedure.

According to the present invention, there is provided a process for producing a composite structure suitable for use in the manufacture of printed circuits and which comprises a carrier layer of aluminium and a covering layer of copper which is tenaciously bonded to the aluminium carrier layer but readily separable therefrom by mechanical means without destroying the integrity of the copper layer, which process comprises (a) cleaning at least one major surface of an aluminium foil to remove surface contaminants therefrom, (b) positioning the aluminium foil in a suitable electrolyte and passing electrical current therethrough so that the foil is rendered cathodic and its surface is activated, (c) positioning the activated foil in a suitable electrolyte and passing electrical current therethrough so that the foil is rendered anodic and a thin layer of aluminium oxide is formed on the surface thereof, and (d) electrodepositing a thin layer

of copper on the anodized surface of the aluminium foil.

The present invention also comprises a composite structure produced by the process according to the invention.

It is preferred that the aluminium foil should be rinsed with water to remove surface contaminants after step (a), step (b) and/or step (c).

Typical aluminium foil used as the carrier layer in the practice of the invention is 1100 or 3000 series aluminium foil (American Aluminium Association designation). However, all that is required of the foil is that it be amenable to being treated cathodically and then anodically so as to form a surface layer of aluminium oxide thereon. The foil used may be in any convenient form, for example, sheet or roll, with it being customary to use it in roll form. The thickness of the foil is not critical except it must be thick enough to carry the covering layer of copper and withstand the high temperatures and pressures experienced during the laminating procedure. In practice, when carrying a 1 to 17 micron thick covering layer of copper, good results have been obtained with aluminium foil having a thickness of from 5 to 10 mils (127-254 microns), with excellent results being achieved with aluminium foil having a thickness of from 2 to 5 mils (51-127 microns). With thicknesses within these ranges, the aluminium layer can be readily stripped from the copper layer without it tearing.

In practice, the surface of the aluminium carrier layer on which the copper layer is to be deposited is first cleaned to remove surface contaminants therefrom. This cleaning can be effected in a number of ways, the preferred method being to use a chemical reagent. For example, the aluminium carrier layer is first treated with an aqueous alkali solution to remove oil and various surface contaminants therefrom. A typical aqueous alkali etchant suitable for this purpose comprises 20 g/l sodium hydroxide, 25 g/l sodium gluconate and 0.1 ml/l tergitol. The required duration of exposure to the etchant depends on the surface contamination of the aluminium carrier layer and is determined empirically.

The so-treated aluminium foil is then, if desired, water rinsed and then positioned in a suitable electrolyte and electric current is directed therethrough in such a manner as to render the foil cathodic so as to activate the surface thereof. The water rinsing is not absolutely required, but improved results are obtained when it is employed. Various electrolytes may be used to effect activation and suitable electrolytes for this purpose are known to those skilled in the art. A particularly preferred electrolyte composition for this purpose comprises, in percent by volume, from 53 to 73% phosphoric acid, from 5 to 25% sulphuric acid and from 12 to 32%

water. The voltage across the foil is suitably from 3 to 15 volts and the current density from 20 to 100 amps/sq.ft. (2.15–10.8 amps/dm²).

5 Following the activation of the aluminium foil surface, the foil is, if desired, water rinsed at room temperature. Any form of non-contaminated water can be used for this purpose.

The foil is then positioned in an electrolyte bath and electric current passed therethrough so that the foil is rendered anodic to form a thin layer of aluminium oxide on its surface. Any suitable electrolyte can be used for this purpose and many such electrolytes are known in the art. A particularly preferred electrolyte for this purpose comprises, in percent by volume, from 53 to 73% phosphoric acid, from 5 to 25% sulphuric acid, and from 12 to 32% water. The voltage applied across the aluminium foil is relatively low and is suitably of from 1 to 15 volts and the current density is from 5 to 30 amps/sq.ft. (0.54–3.23 amps/dm²). By following this technique, a relatively thin surface layer of aluminium oxide is formed on the foil which provides a suitable surface for accepting electrolytically deposited copper.

The anodised aluminium foil is then, if desired, water rinsed and copper is then electrolytically deposited on the anodised surface by conventional techniques. A typical electrolyte for this purpose is, for example a standard pyrophosphate bath which typically contains 22.5 g/l of copper, 160 g/l of pyrophosphate and has a pH of about 8.3. Electrodeposition of the copper is effected by operating the bath at a temperature of about 135°F (57.2°C) at a voltage of about 3 volts and a current density of about 30 amps/sq.ft. (3.23 amps/dm²).

In the manufacture of a composite structure intended for use in the fabrication of printed circuits, it is common to electrodeposit a layer of copper having a thickness of from 1 to 17 microns on the aluminium carrier material. However, when it is desired to produce a foil which can be used to form a printed circuit while minimizing so-called "undercutting" problems, it is preferred that the copper layer should have a thickness of from 5 to 10 microns.

The process according to the invention can be carried out in either a batch or continuous manner. That is, aluminium foil can be continuously fed from a roll into a chemical cleaning solution, from the cleaning solution into an optional, but preferred, water rinse, from the rinse into an electrolyte solution for cathodic activation, from the electrolyte solution into an optional, but preferred, water rinse, from the water rinse into an electrolyte solution to anodically treat the surface of the foil, from the anodic treatment bath into an optional, but preferred, water rinse, and then directly into a copper electroplating bath. Or, if de-

sired, each one of the above-described sequential steps can be carried out individually.

In order that the invention may be more fully understood, the following example is given by way of illustration.

Example

A roll of 1100 Series (American Aluminum Association designation) aluminium foil having a width of 54 inches (137 cms) and a thickness of 75 microns was directed into an aqueous cleaning bath containing 20 g/l of sodium hydroxide, 25 g/l sodium gluconate and 0.1 ml/l of tergitol. The feed rate was adjusted so that any given segment of the aluminium foil was exposed to the cleaning bath for up to about 3 minutes. The bath was operated at a temperature of 105°F (40.6°C). Upon emerging from the cleaning bath, the aluminium foil was rinsed in flowing water for approximately 1 minute at room temperature. The aluminium foil was then directed into an electrolyte bath containing, in percent by volume, 63% phosphoric acid, 15% sulphuric acid, and 22% water. Electric current was passed through the foil in such manner that the foil was rendered cathodic. The voltage was 7 volts and the current density was 50 amps/sq.ft. (5.4 amps/dm²). The cathodically activated aluminium foil was then rinsed in water for about 2 minutes at room temperature.

The rinsed aluminium foil was then directed into an electrolyte bath containing, in volume percent, 63% phosphoric acid, 15% sulphuric acid, and 22% water. Electric current was passed through the foil in such manner as to render it anodic and form a thin layer of aluminium oxide on its surface. The voltage used was 11 volts and the current density was 20 amps/sq.ft. (2.15 amps/dm²).

The anodised aluminium foil was then water rinsed and directed into a conventional aqueous copper electroplating bath which contained 22.5 g/l of copper and 160 g/l pyrophosphate and had a pH of about 8.3. The bath operating temperature was about 135°F (57.2°C). The plating voltage was about 3 volts and the current density was about 30 amps/sq.ft. (3.23 amps/dm²). The foil emerging from the bath had a surface layer of copper thereon having a thickness of about 2.5 microns. This material was then overplated in a conventional manner to a final thickness of about 5 microns and a nodularizing surface treatment was then applied thereto, as taught in U.S. Patent 3,585,010.

The composite material thus obtained was then bonded in a conventional manner to an insulating substrate. The insulating substrate was composed of glass fibre reinforced epoxy resin. The lamination was effected by applying pressure to the sandwich type structure while heating it to a temperature of about 400°F (204°C). After cooling, the carrier layer of

aluminium was then readily removed from the laminated structure by simple mechanical stripping without deleteriously affecting the surface layer of copper. The force required to remove the aluminium carrier layer was about 0.1 lb per inch (0.018 kg/cm) of width. The desired circuit was then etched into the surface layer of copper by conventional techniques.

- 10 In contradistinction thereto, a laminated structure was prepared using the same general procedure described above, except the carrier layer of aluminium was not treated cathodically before it was anodized and a layer of copper electrolytically deposited thereon. The force required to remove the aluminium carrier layer from this composite varied from greater than 2.0 lbs per inch width (0.36 kg/cm) to unpeelable.
- 20 In the manufacture of printed circuit boards, many laminate materials require high laminating temperatures for prolonged periods of time to fully cure the resin matrix. Proper curing is necessary to obtain the desired electrical, mechanical and chemical properties in the laminate. When temperatures of about 400°F (204°C) are utilized, while the copper layer becomes tenaciously bonded to the substrate, difficulties are experienced in that the carrier layer of aluminium is not readily strip-
30 pable from the copper layer. In contrast, when the technique of the present invention is used, laminating temperatures of about 400°F (204°C) can be used to obtain a tenacious
35 bonding between the copper layer and the insulating substrate and the carrier layer of aluminium can still be readily removed from the copper layer by simple mechanical stripping techniques. In addition, and perhaps more
40 importantly, when the technique of the present invention is used, a laminate is obtained which has the desired electrical, mechanical and chemical properties.

45 CLAIMS

1. A process for producing a composite structure suitable for use in the manufacture of printed circuits and which comprises a carrier layer of aluminium and a covering
50 layer of copper which is tenaciously bonded to the aluminium carrier layer but readily separable therefrom by mechanical means without destroying the integrity of the copper layer, which process comprises (a) cleaning at least
55 one major surface of an aluminium foil to remove surface contaminants therefrom, (b) positioning the aluminium foil in a suitable electrolyte and passing electrical current there-
60 through so that the foil is rendered cathodic and its surface is activated, (c) positioning the activated foil in a suitable electrolyte and passing electrical current therethrough so that the foil is rendered anodic and a thin layer of aluminium oxide is formed on the surface
65 thereof, and (d) electrodepositing a thin layer

of copper on the anodised surface of the aluminium foil.

2. A process according to claim 1, in which the aluminium foil is water rinsed after
70 step (a) to remove surface contaminants therefrom.
3. A process according to claim 1 or 2, in which the aluminium foil is water rinsed after
75 step (b) to remove surface contaminants therefrom.
4. A process according to any of claims 1 to 3, in which the aluminium foil is water rinsed after step (c) to remove surface contaminants therefrom.
- 80 5. A process according to any of claims 1 to 4, in which the electrolyte used in step (b) comprises, in volume percent, from 53 to 73% phosphoric acid, from 5 to 25% sulphuric acid, and from 12 to 32% water.
- 85 6. A process according to any of claims 1 to 5, in which the electrolyte used in step (c) comprises, in volume percent, from 53 to 73% phosphoric acid, from 5 to 25% sulphuric acid, and from 12 to 32% water.
- 90 7. A process for producing a composite structure according to claim 1, substantially as herein described in the Example.
8. A composite structure when produced by the process claimed in any of the preceding
95 claims.

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- 85 6. A process according to any of claims 1 to 5, in which the electrolyte used in step (c) comprises, in volume percent, from 53 to 73% phosphoric acid, from 5 to 25% sulphuric acid, and from 12 to 32% water.
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