

[72] Inventor **Walter A. McKean**
Colonia, N.J.
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[73] Assignee **Circuit Foil Corporation**
Bordentown, N.J.

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Primary Examiner—John H. Mack
Assistant Examiner—T. Tufariello
Attorney—Lane, Aitken, Dunner & Ziems

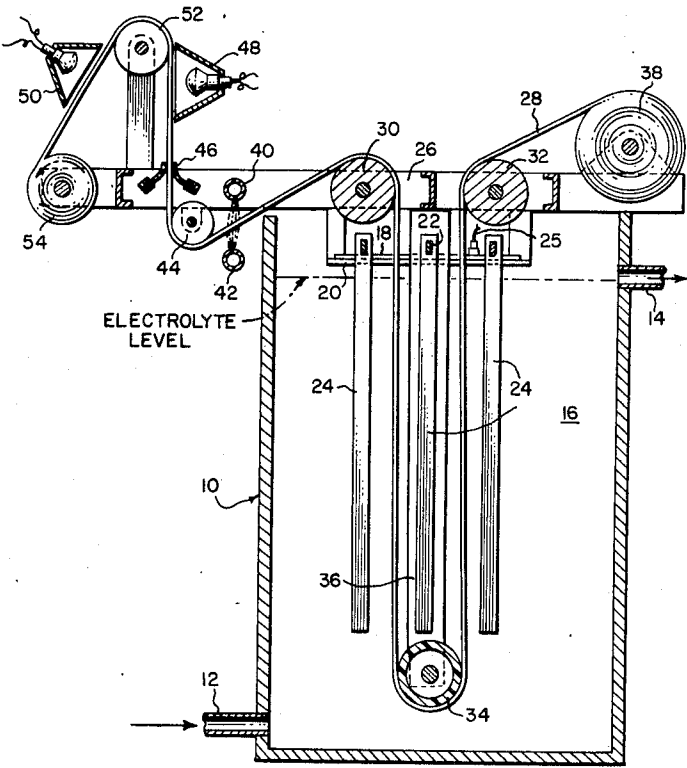
[54] **STAINPROOFING PROCESS AND PRODUCTS
RESULTING THEREFROM**
6 Claims, 1 Drawing Fig.

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ABSTRACT: An electrolytic process for imparting stain resistance to sheet copper comprising rendering the copper sheet cathodic in an electrolytic cell containing an aqueous electrolyte containing about 0.4–0.8 grams/liter of hexavalent chromium ions and subjecting said foil to a current density of about 2–4 amps/ft.² for about 6–8 seconds. Products resulting therefrom.



STAINPROOFING PROCESS AND PRODUCTS RESULTING THEREFROM

BACKGROUND OF THE INVENTION

One of the problems with which manufacturers of copper foil (both of the electrolytic and rolled variety) are faced is the staining of the copper foil between the time of shipment and the time of use by the ultimate purchaser. This staining results from the exposure of the copper to normal atmospheric and other conditions and, particularly for applications of the copper foil in critical areas such as printed circuitry, is an extremely undesirable characteristic.

In the past, various suggestions have been made for stainproofing copper foil. While a number of the approaches used in the past have served to stainproof such foil, one of the difficulties related to the use of such techniques is that they have created one or more collateral problems negatively affecting the desirability of the treated copper for use in printed circuit applications and the like. Such problems include:

- a. a decrease in the bond strength of the stainproofed foil;
- b. an increase in the etching resistance of the foil;
- c. a decrease in the solvent resistance of the adhesive/treatment interface; and/or
- d. a decrease in the solderability of the shiny side of the foil.

SUMMARY OF THE INVENTION

In accordance with the present invention, a novel stainproofing technique is provided which provides to copper foil a finish having superior tarnish and oxidation resistance but which does not deleteriously affect such foil in any of the manners described above. This technique involves the use of an aqueous electrolyte under critical conditions of hexavalent chromium ion concentration, cathode current density and treatment time.

OBJECTS OF THE INVENTION

It is accordingly an important object of the present invention to provide a novel stainproofing technique useful in stainproofing copper foil rendering such foil particularly adapted for use in printed circuit applications.

It is a further important object of the present invention to provide an improved electrolytic stainproofing technique for stainproofing copper foil involving the use of a novel electrolyte bath as well as products resulting therefrom.

These and other important objects and advantages of the present invention will become more apparent as this description proceeds.

DESCRIPTION OF THE DRAWINGS

The FIGURE is a front elevation, partly in section, illustrating an electrolytic tank for carrying out the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As previously noted, the material to be subject to the improved stainproofing treatment of the present invention is sheet copper. While electrodeposited copper foil is preferred (particularly for printed circuit applications), other types of sheet copper (such as rolled foil) may be used.

The preferred method for stainproofing such foil is to use an elongated sheet of such foil and to pass such elongated sheet through an appropriate electrolyte using an apparatus such as is illustrated in the FIGURE. The apparatus illustrated therein comprises a tank 10 containing an electrolyte inlet 12 and electrolyte outlet 14 by means of which electrolyte 16 respectively enters and is withdrawn from tank 10. The positive bus bar 18 is secured to one longitudinal top edge of tank 10 by means of insulating strip 20. Supported on the bus bar 18 and insulating strip 20 by means of copper bars 22 are a plurality of anodes 24. These anodes 24 are shown in the form of thick, insoluble planar lead plates (which may appropriately be also made of stainless steel). A terminal lead 25, adapted to be

connected to the positive terminal of a power source (not shown), is connected to the bus bar 18. A support frame 26 is mounted on the tank 10.

In order to guide a sheet of copper 28 to be stainproofed, two upper electrically connected idler rollers identified by the numbers 30 and 32 are mounted on and are in electrical contact with the support frame 26, and a polyvinyl chloride idler roll 34 is rotatably mounted on a stainless steel bar 36 which, in turn, is connected to the supporting frame 26 at its upper end. By virtue of the electrical contact between rollers 30 and 32 and support frame 26, and by connecting the latter to the negative terminal of a power source (not shown), copper sheet 28 may be rendered cathodic.

The continuous sheet of copper 28 which is to be stainproofed is shown fed from a supply spool 38 mounted on the support frame 26, over the first upper idler 32 and into the electrolytic bath 16. The continuous sheet 28 is guided into and out of the electrolyte 16 in serpentine fashion by means of the idler roller 34 at the bottom of the tank 10 and the upper idler roller 30. As the stainproofed sheet 28 emerges from the electrolytic tank 10, it passes by a pair of nozzle elements 40 and 42 which are connected to a source of wash solution (not shown) to permit the sheet 28 to be spray washed on both sides. The stainproofed sheet of copper is then fed across idler roller 44, past a squeegee device 46 which removes any excess material, past a pair of infrared lamps and an idler roller 52, 48 and 50 to dry the stainproofed material and finally to the take-up roll 54 which is provided with a suitable drive mechanism (not shown) which provides the necessary force to draw the sheet of copper 28 through the system.

By passing the copper foil through the system in the manner indicated, the matte and shiny surfaces of the foil will receive an electrochemical treatment and will have stain resistance imparted thereto.

As will be apparent, electrolytic tank 10 can be enlarged and additional anodes 24 added to increase the amount of exposure of the moving sheet of foil to electrolytic treatment, though for the purpose of the present invention, a 3-anode system is quite adequate to expose the foil to the critical treatment time mentioned below.

The electrolyte employed in the present invention is an aqueous electrolyte containing hexavalent chromium ions which is preferably substantially free of any impurities. Such an electrolyte may conveniently be formed by dissolving chromium trioxide (CrO_3) in water to form chromic acid. This aqueous solution must contain 0.4–0.6 grams/liter of hexavalent chromium ions (determined as CrO_3). As the copper foil passes through the electrolyte, it should be subjected to a cathode current density of about 2–4 amps/ft.² for about 6–8 seconds.

When foil is subject to conditioning as set forth above, the foil has a remarkable degree of resistance to oxidation and tarnishing as measured by several accelerated staining procedures (immersion in a sulfide test solution and a humidity exposure test), while not suffering any of the disadvantages previously noted as being associated with prior art techniques.

The particular hexavalent chromium ion concentration, cathode current density and exposure time are critical in the carrying out of the process of the present invention. More specifically, when hexavalent chromium ion concentrations, cathode current densities and exposure times below the aforementioned lower limits are used, adequate stain protection is not provided to the copper foil; similarly, the use of hexavalent chromium ion concentrations, cathode current densities and exposure times above the aforementioned upper limits hinders etching of the foil in printed circuit applications.

In a specific example of the process of the present invention, one ounce copper foil (which had been previously electrochemically treated to improve bond strength) was passed in serpentine fashion in the manner indicated above past insoluble lead anodes in an aqueous chromic acid electrolyte containing 0.5 grams/liter of hexavalent chromium ions (determined as CrO_3). The electrolyte was at a temperature of 25°

C., the cathode current density was 3 amps/ft.² and the copper was immersed in the electrolyte for 7 seconds. The resulting copper foil has excellent stain resistance as measured by a standard sulfide stain resistance test and passes a standard etchability test employed for printed circuit applications.

The standard sulfide stain resistance test involves the immersion of the foil in a filtered solution of 5 grams/liter of Zonax Oxidizing Salt (a proprietary material produced by W. Canning Co. in Birmingham, England which is likely an ammonium polysulfide compound) in distilled water. The solution is maintained at room temperature without agitation.

Stain resistance is proportional to the time after immersion that an overall black film is produced on the shiny surface of the foil. Untreated foil will stain in less than 5 seconds, ordinary prior art stainproofed foil in 15 to 30 seconds, while foil stainproofed in accordance with the process of the present invention may last over 5 minutes without staining.

The standard etching test described above is as follows:

A. Solutions

1. Etch solution (5 percent ferric chloride in water) a standard 42° B. ferric chloride etch solution such as Hunt's RCE in the ratio of 1 part concentrate plus 7 parts water.
2. Post-etch cleaning solution 10 percent by volume of concentrated hydrochloric acid in water.

B. Procedure

Immerse the sample to be tested in the 5 percent etch solution at room temperature and without agitation for 60 seconds. Remove from the etch and place in the 10% hydrochloric acid solution for 60 seconds. Remove and wash in running water. Dry and examine.

A properly etched specimen will exhibit a uniform matte

surface of a reddish pink color. Non-etchability shows shiny streaks or areas in the immersed portion. Extreme cases of etch resistance appear indistinguishable from the unetched areas.

This test applies only to the shiny surface of electrodeposited foil.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed is:

1. An electrolytic process of imparting stain resistance to sheet copper comprising rendering said copper sheet cathodic in an electrolytic cell containing an electrolyte comprised of an aqueous solution containing about 0.4 to 0.6 grams/liter hexavalent chromium ions (determined as CrO₃) and subjecting said sheet copper to a current density of about 2 to 4 amps/ft.² for about 6 to 8 seconds.

2. A process as defined in claim 1 wherein said copper is copper foil.

3. A process as defined in claim 1 wherein said electrolyte is substantially free of impurities.

4. A process as defined in claim 1 wherein said electrolyte contains dissolved chromium trioxide.

5. The product of the process of claim 2.

6. The product of the process of claim 1.

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