ABSTRACT

«Galvanic coatings in instrument manufacturing. Development of the technological process of the previous galvanic copper coating of printed circuit boards»

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The purpose of this project is to develop a process of previous galvanic copper coating of printed circuit boards, with a productivity of 100,000 units/year.

Printed circuit boards (PCBs) are the main component, providing the work of all units of electronic equipment, devices or components, are of great importance in the production of electronic equipment. The PCB is an insulating base, on one or both sides of which there are conductive strips of metal in accordance with the electrical circuits. The PCBs are intended for installation of electric radio elements, as well as for switching of separate units of devices among themselves. The use of PCBs can significantly reduce the overall dimensions of devices, reduce their metal capacity, facilitate assembly and adjustment of equipment, and improve their performance. Printed boards are widely used for the manufacture of various electronic equipment, radar equipment, airborne equipment, aircraft, rockets, spacecraft, etc.

An important operation in the manufacturing of PCBs is the process of previous galvanic copper coating. The copper coating should provide high-reliability electrical connection of the elements of the board in a thermal shock (rapid heating and cooling of the board in the temperature range -20...240˚C).

It is a copper coating that provides all of these properties, since copper has good electrical conductivity and price-quality ratio, and therefore it has become most widely used as the main material when conducting conductive paths.

In connection with the use of PCBs in ultrasound equipment, in avionics, space technology, further improvement of the process of their manufacturing is to reduce the cost of the metal to obtain the same properties, reduce the width of conductors, reduce the total weight of the final product, as well as improve their thermal properties, such as increasing the operating temperature and resistance to thermal shock when working in difficult environments.

Printed boards (PCBs) can be made on ceramic, on hard (hard) and on the flexible dielectric basis. Solid-state boards are divided into single-layered and multilayer. Single-layer boards can be one-sided and double-sided with transition joints using metalized holes. Flexible boards are divided into one-sided and double-sided interconnecting devices.

Multilayer PCBs consist of arranged alternating thin insulating layers with applied conductive drawings on them. Electrical connections in multilayer boards are carried out using metalized through holes.

Unilateral PCBs are the most common and are used for the production of simple radio-electric equipment, and two-way transceivers with transient connections, for the production of more sophisticated radio-electronics devices.

Multilayer PCBs are used as commuting nodes in the manufacture of complex radio-electric equipment and computer facilities.

Two-sided PCBs have a conductive pattern on either side of the dielectric or metal base. The electrical connection of the layers of the printing assembly is carried out by means of metallization of the openings. Double-sided PCBs have higher mounting density and reliability of joints. They are used in measuring technology, control systems, and automatic control. Location of the elements of the printed assembly on the metal basis allows solving the problem of heat transfer in the high-current and radio-transmitting equipment. In the manufacture of PCBs, depending on their design features and scale of production, different versions of technological processes, which use numerous chemical-technological operations and machining operations, are used.

The PCBs have the following requirements:

1. High accuracy of the layout of the conductive pattern
2. The large magnitude of the resistance of the dielectric
3. High mechanical strength
4. Good soldering ability, special after prolonged storage.

The accuracy of the location of the conductive pattern is regulated by the requirements of DSTU 2646-94.

General material requirements:

– high dielectric properties;
– high chemical resistance;
– good mechanical processing ability;
– Sufficient mechanical stability;
– good heat resistance;
– independence of mechanical and electrical properties from climatic influence;
– Minimal warping;
– safe to fire;
– low cost.

For PCB production, foil dielectrics are commonly used, and rarely – unfiltered.

In the elaborated project as a material for making PCBs, it is supposed to use foamed glass fiber of the brand SF-2-35.

Thus, the most common and promising is the basic positive combination method, which is characterized by the fact that drilling of all openings under metallization is performed on the prepackaging of the board prior to the application of a protective relief. That is why this method is chosen for the developed project.

It involves the following technological operations:

1. Input control of the foil dielectric;

2. Manufacturing of PCBs' billets;

3. Manufacturing of base or fixing holes;

4. Boring of openings that are subject to metallization on numerically controlled machine tools;

5. Chemical-mechanical preparation of the surface of the workpiece and hydro abrasive cleaning of the openings;

6. Chemical binder to a thickness of 1 μm or direct metallization of dielectric in openings;

7. Pre-galvanic copper to a thickness of 4 – 7 μm;

8. Application of the protective relief to the free space of the workpiece;

9. Galvanic flux of conductive pattern with a thickness of 25 microns or more in openings;

10. Galvanic application of tin on a conductive pattern in the thickness of 5...7 micrometers;

11. Removal of the protective relief from the free places of the workpiece;

12. Digestion of copper from vacant places of work;

13. Chemical etching of tin from conductive pattern;

14. Application of a protective mask on the entire surface of the board, excluding soldering places;

15. Application of the finish coating to the places of soldering;

16. Depending on the complexity of the conductive drawing – electro-control;

17. Marking inscriptions;

18. Processing of circuit board procurement;

19. Quality control of PCBs

Copper electrolytes used in the production of PCBs should provide:

– high scattering ability and uniform deposition of copper layer at a ratio of thickness of a layer on a surface and on a wall of a hole from 0,8:1 to 1:1;

– uniform distribution of copper on the surface of the board, regardless of its size and pattern of conductors;

– obtaining a uniform fine crystalline coating;

– precipitation of a plastic, sufficiently strong layer with low internal stresses;

– a rather high rate of copper deposition.

Of the acidic electrolytes of copper, the most widely used sulfate electrolytes, characterized by simplicity of the composition, cheapness, chemical resistance and permissible high density of current. The current output in these electrolytes is close to 100% and almost does not change with the change in current density. The disadvantages of acidic electrolytes are their insignificant scattering ability and a ruder structure of sediments compared with alkaline electrolytes. In order to significantly increase the efficiency of copper processes in acidic electrolytes, formulations with additive components have been developed that give gloss and equalizing effects.

Given the fact that sulfuric acid electrolytes are available and relatively cheap, easy to operate, easily prepared and adjusted, the developed project proposes to use an electrolyte of the following composition:

Copper sulfuric acid (hydrate) (copper) 15 g/l

Sulfuric acid (density = 1,84 g/cm^3) 220 g/l

Chlorine-ion (introduced as sodium chloride) 80 mg/l

Grundeinebner Cupracid BL-CT 15 ml/l

Glanzzusatz Cupracid BL 0.5 ml/l

1. The temperature of the electrolyte should be 15 – 25 °C. Within the specified limits, the quality of the coating and the robustness of the electrolyte do not depend on temperature. An increase in temperature above 25 °C leads to an increased cost of a brightening additive, reducing the dissipation capacity and reducing the gloss coating. Under strong cooling (less than 15 °C), the current density decreases, which leads to a decrease in the plasticity of the coating.

2. The mixing of the electrolyte is carried out by the movement of cathode bars with a linear speed of 0.8-1.6 m/min. Mixing with bubbling increases the dissipation capacity.

3. The cathode current density is 2-3 A/dm^2 (optimal 2.5 A/dm^2). The density of the anode current is 1.5 A/dm^2. In the region of low current density, matte coatings are deposited.

4. Cathode current output is close to 100%.

5. The deposition rate of the coating is about 26 μm/h at a current density of 2 A/dm^2.

Daily periodic filtration of the electrolyte (filtering speed of 5 rpm; filter material of polyspun 5-10 microns). Filters are used for removal of photoresist fragments, filaments of fiberglass from glass fiber, dust from air and particles of anode sludge

The high quality of coatings is achieved by the use of copper anodes of the AMF brand, doped with phosphorus. Used cold-rolled anodes, which are manufactured according to GOST 760-70, or hot-rolled (TU 48-21-5045-76) in the form of plates. It is possible to use lump anodes in titanium baskets.

Phosphorus additive has three functions:

1. Contributes to the deoxidation of copper grains when rolling anodes, preventing sludge formation;

2. Single-walled copper, formed near the anodes, binds to an insoluble Cu_3P compound that forms a dark anode film. This film does not interfere with the anode formation of Cu^{2+}, but at the same time prevents the disproportionation reaction;

3. The film prevents the anode oxidation of surfactants.

For preventing the accumulation of anode sludge, a constant or periodic filtration of the electrolyte is required.

The anodes are used in cases made of a special acid-resistant, fully synthetic material.

In this project, polypropylene baths with a thickness of 20 mm, with five ribs of stiffness are selected. The bath has 2 anodes and a pendant. To mix the bath is equipped with bubbling. Overall dimensions of the bath are chosen 1040x670x820 in accordance with the current standard (GOST 23738-85).

The main parameters associated with the automatic line debugging are:

• temperature;

• level;

• voltage;

• amperage;

• pH.

In automated systems, temperature measurement is carried out on the basis of the physical properties of bodies that functionally associated with the temperature of the latter. The process of bending is carried out at room temperatures of 15 ... 25 ° C. The temperature can be measured with different types of thermometers.

In the process of applying copper coating, the composition of the electrolyte, its volume, and also the pH of the solution may change. The volume of the electrolyte may vary when sprayed during unloading of parts.

With regard to changes in the composition of the electrolyte and pH, this fact can lead to a deterioration of the structure of the sediment and its uniformity, which adversely affects its quality. That is why the constant composition of the electrolyte, its level and pH should be automatically maintained.

The aim of the project is to produce 100,000 PCBs per year. The equipment was chosen in such a way that during one cycle of operations one blank was produced, on which 8 PCBs were placed. Therefore, the workshop must produce 12,500 pieces per year.

The optimal TMWI for PCB production is synchronized with the rhythm of 15.29 minutes, because to ensure the planned production of products requires a minimum amount of equipment that will save significant money and reduce the cost of finished products.

To ensure the planned production of blanks, the following equipment is required:

• chemical degreasing bath – 1 unit;

• cold wash bath – 1 unit;

• bath for preliminary galvanic copper – 1 unit;

• drying chamber – 1 unit.

Given the automation of operations, one change is enough to:

• One specialist in electroplating, which controls the concentration of electrolyte components in the bath, voltage and current in the baths;

• The installer, responsible for assembling the blanks at the beginning of the site and their dismantling after passing the process;

• A line operator that monitors the movement of the cathode rod along the line and the time of operations.

As can be seen from the technical and economic indicators, the area of the previous galvanic copper in the production of printing machines is cost-effective, since the investment return period is 2.94 years.

Galvanic production is one of the most dangerous sources of environmental pollution, mainly surface and groundwater, due to the formation of large amounts of wastewater containing harmful impurities of heavy metals, inorganic acids and alkalis, surfactants and other harmful compounds.

Compounds of metals, which are deposited by sewage of galvanic production, have a very harmful effect on the ecosystem of the reservoir – the soil – the plant – the animal world – a man.

Many chemical substances entering the environment, including in the reservoir, and through drinking water in the human body, in addition to toxic effects can have a carcinogenic effect and mutagenic.

In the developed technological process of the previous galvanic copper of PCBs the main source of environmental pollution, in particular reservoirs, is copper.

Copper refers to heavy metals, compared to other heavy metals (Cd, Cr, Pb) is less toxic to humans and animals, but adversely affects aquatic organisms, inhibits biological purification of water.

Influence on man and warm-blooded animals. The deadly dose for a person is 10 g/kg of body weight, the dose of 60 – 100 mg/kg of weight causes nausea, vomiting, gastroenteritis, and the dose of 10 – 30 mg/kg of the mass does not have a toxic effect with the consumption of copper inside for several weeks.

Influence on aquatic organisms. At the concentration of copper 0.01 mg/l, the processes of self-cleaning of water bodies are inhibited. At a concentration of 0.4 – 0.5 mg/l copper is detrimental to the microflora and inhibits the biological processes of wastewater treatment, inhibits the reproduction of microorganisms; At copper concentration of 1.0 mg/l, the processes of aerobic sewage treatment with active sludge are noticeably inhibited, the amount of oxidized nitrogen in sewage is reduced, and the formation of active sludge is delayed.

Influence on crops. Getting with wastewater into the soil under watering, copper is cumulative with soil and plants, detects a harmful effect on them, starting with a concentration of 0.1 mg/l.

To return to the production of copper, which is discharged with sewage and "forbidden" along with sediment, there is a simple and economical method of extracting it from solutions – contact restorations (cementation) on the surface of the iron. Copper is released in the form of a metal powder, and the ions of iron pass into the solution.

After cementation, the solution contains ions of iron and copper, the ratio of which depends on the duration of the reaction. When neutralizing this solution, an alkaline reagent forms a volumetric precipitate of copper and iron hydroxides. The resulting sediment is strongly dewatered, so it is difficult to separate from the liquid phase and in the future, as a rule, is not used. After sending to the landfill, this sediment is in contact with surface and groundwater and thus contaminates the environment.

The obtained hydroxides precipitate can be converted into an insoluble ferrite iron with high magnetization in one stage. Since copper is a metal that is close to iron in its basic physical and chemical properties, it is possible to carry out the synthesis of copper ferrite $CuFe_2O_4$ with a molar ratio of copper to iron of 1: 2 at appropriate concentrations and similar conditions. Successful flow of the process is facilitated by similar pH values deposition of $Cu(OH)_2$ and $Fe(OH)_2$. As a result, when they are coalescented with alkali, close interaction of particles is achieved, which greatly accelerates the formation of the crystalline structure of copper ferrite, with subsequent oxidation of Fe (II) in (III) oxygen to the air. It should be noted that since the solution in its composition is approximately equal to the molar ratio of copper and iron ions (II), then to obtain the copper ferrite in the solution it is necessary to add iron sulfate (II) 10% in an amount that provides the molar ratio of copper and iron as 1: 2.

To obtain a sediment with a minimum volume and significant sedimentation and ferromagnetic properties at minimum residual concentrations of iron and copper, it is necessary to create the appropriate conditions: temperature above 60 ° C, pH 9. At pH 9, the formation of ferrite is significantly slowed down, since the rate of iron oxidation (II) in iron (III) increases with increasing pH. The process of ferrite formation can be accelerated more than twice by adding in the solution of $CuFeO_4$ crystals of 0.05 g/l. After cooling and washing with distilled water, the ferromagnetic precipitate is separated by filtration and its analysis is carried out to determine the structure and subsequent use. Thus, a ferromagnetic suspension can be dispensed with flushing waste water for purification purposes. The crystalline lattice of the resulting particles has numerous defects, and hence the developed surface. When mixing this suspension with washed wastewater in the drainages, heavy metal ions are adsorbed on the surface of the crystals. Removal from the water of particles with adsorbed contaminants can be carried out by magnetic separation. The efficiency of water purification depends on the value of the pH of sewage and the properties of crystals, which are determined by the conditions of their formation. In addition, copper ferrite is widely used in many fields of technology, in particular in radio and electronic equipment.

The project provides for the creation of appropriate conditions for the formation of copper ferrite in the process of purifying acid-alkali sewage containing copper, with a view to its further use.

Sulfur effluents containing copper enters the tank, where they are fed to the cementant, filled with iron shavings. Copper is released in the form of a metal powder, and the solution is enriched with iron ions (II). Once the ratio of iron and copper ions in the solution exceeds the value required for passing the process, it is poured into the reactor. Cementur is filled with water and by bubbling air the copper is separated from the chips. Water, along with copper, is merged into a centrifuge. After dehydration, copper is sent to non-ferrous metal processing enterprises.

In the reactor, the formation of a ferromagnetic mixture occurs in compliance with the above conditions of the process. The resulting precipitate is separated from the sewage in the settling tank, separated from the solution and enters for further processing and use.

Water from the tank is undergoing a three-stage cleaning. On the mechanical filter, there is an iron removal, the sorption of residual impurities occurs on the activated carbon filter, carbon dust is removed on the mechanical filter. Water free from ferromagnetic particles fed to the reverse osmosis membrane, which completely cleared, and as a result received demineralized water that returns to the production and preparation of electrolyte solutions.

The project developed a manufacturing process of previous galvanic copper plating of PCBs. Precipitation is performed in sulfate electrolyte in the cathode current density of 2 A/dm^2, temperature 18 – 25 °C, with optional swing suspension with the blank PCB. The project conducted design and engineering calculations developed a scheme of automatic regulation of copper plating. Completed feasibility calculations proposed scheme sewage treatment reagent method, analyzed the harmful and dangerous production factors and proposed safety measures and safety.

Key words: PCB, copper, production, electrolyte, water, galvanic, coating, sulfate, developing, anodes, electrical, manufacturing, wastewater, metallization, automatic, layer, cementation.