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The manufacture of capacitors calls upon a very broad range of technical expertise. The article which follows examines the chemical considerations involved in making a change in electroplating electrolyte for finishing chip multilayer ceramic capacitor terminations. Larry Helton, the author, is an expert in electrochemistry, and a Technical Associate in KEMET's Technology Department.

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A New Tin Electroplating Bath for KEMET Multilayer Ceramic Capacitors

by Larry Helton

Introduction

As the demand increases for smaller and smaller surface-mount multilayer capacitors with high reliability and low manufacturing costs, KEMET has strived to optimize its process. One improvement has been the change in the electroplating process, which has resulted in greater control of the process and reduced waste.

Evolution of Electroplating

Originally, surface-mount multilayer ceramic capacitors were terminated with a silver-palladium alloy-glass frit composite.[1] However, solder leaching of the silver-palladium during circuit assembly was a serious problem. In the early 1970s, base-metal barrier layers started to be plated over silver or silver-palladium terminations. These evolved into the nickel barrier layers overcoated with tin or tin-lead solder plate that are currently in common use (Figure 1).

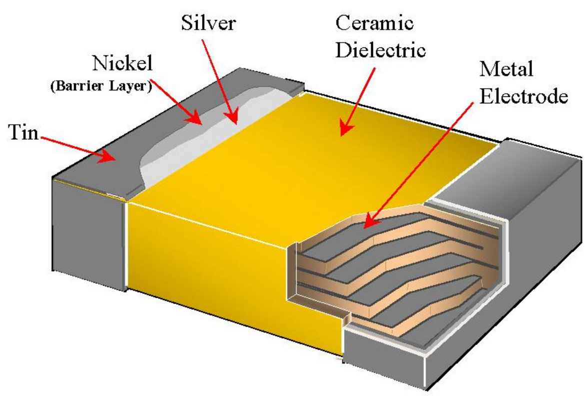

Figure 1. Typical Monolithic Ceramic Chip Capacitor

KEMET's multilayer ceramic capacitors have silver terminations that are electroplated in rotating barrels containing a cathode (negative) connection, conductive media such as small metal balls, and the chip capacitors. First, approximately 100 microinches of low-stress nickel are plated onto the chip terminations. Because nickel oxidizes at room temperature and can then only be soldered with highly activated fluxes, another metal is needed to maintain solderability. In KEMET's process this metal is tin; about 150 microinches of tin are electroplated onto the nickel-plated terminations.

Problems with the Traditional Tin Bath

Tin exists in two ionized forms: stannous tin (Sn^{+2}), which is relatively soluble; and stannic tin (Sn^{+4}), which readily forms insoluble compounds. Soluble stannous tin is the desired form for plating solutions; stannic tin contamination greatly decreases the capacitor's surface insulation resistance in high humidity. Unfortunately, in KEMET's traditional tin bath process, nascent oxygen was generated at the anode during plating, oxidizing some of the stannous tin into insoluble stannic tin. The stannic tin remained as particles too small to filter in the plating bath. These particles adhered to the ceramic surfaces of the capacitors during plating and could not be removed by subsequent rinsing. In high humidity, stannic tin contamination increases the rate of decay in surface insulation resistance. Frequent changes of the tin plating bath were required to minimize stannic tin contamination A second drawback to the traditional bath was the complexity of organic additives. All functional tin bath formulations have organic grain refiners (usually proprietary) to produce solderable deposits. Without these refiners, the tin deposit is grainy and solders poorly. The organic additives in our previous bath were too complex to control by direct analytical methods, so process control depended on analyzing deposit characteristics.

The high acidity (0.2 pH) of the previous bath also created solubility problems. Glass secondary phases on the ceramic surfaces of the capacitors were at times soluble in the plating solution, so the sintering assists added to the dielectric were limited by the plating solution. Also, if the glass bonding additive were inadvertently exposed to the plating solution without the protection of plating bias voltage, etching of the silver termination occurred.

A final problem was that as technology evolved, the demand for smaller chips made the process window for the previous plating process very tight. As chip size popularity shifted from 1206 to 0805 and on to 0603, the process optimums required for smaller chips progressively restricted overall productivity.

[1] US Patent #3,612,963 issued Oct. 12, 1971 – Assigned to KEMET Electronics Coporation

KEMET's New Tin Bath

The problems with the traditional bath clearly defined the requirements for a new plating bath. A technical survey of specialty chemical suppliers yielded a bath that fulfilled all of these requirements. The new bath is formulated with complexing agents that chemically bond only with stannous tin. These agents keep the tin in its stannous state, preventing the transformation into stannic tin. This factor alone has added stability and longevity to the bath life and eliminated the surface insulation resistance failures of plated capacitors.

The plating electrolyte is an organic acid, so it has a high pH (between 3 and 4, which is more than 103 less acidic than the previous bath). Conductivity remains high because of the addition of "conductivity salts": organic salts with cations that do not compete with the stannous ions for deposition at the cathode.

The new tin bath gives KEMET the ability to analyze the organic additive, so the performance of the plating solution is now predictable. Another benefit is the greater process latitude permitted by controllable organic additives; as chip size decreases, KEMET can continue to improve capability and productivity.

Table 1 compares the characteristics of the two plating systems.

Characteristic	Old Bath	New Bath
pH	0.2	3 – 4
Tin	Sn^{++}	Sn^{++} in Organic Complex
Direct Analysis of Bath Organics	Not Analyzable	Analyzable
Stable	NO	Yes
Bath Life	2 Weeks	1½+ years
Productivity	1	1½ X
Waste Treatment	Simple	Requires Additional Steps

Waste Treatment

The same characteristic that makes the new tin bath so stable also creates a new waste treatment problem. When the plating cycle ends, the capacitors are removed from the plating bath, inevitably with a certain amount of tin solution adhering to their surface. To remove this excess solution, the capacitors are rinsed in deionized water. The dissolved metal that remains in the deionized water from this step requires a waste treatment process. This process removes the dissolved metals by precipitation.

The new tin bath has complexing agents that are insensitive to changes in pH. Therefore, the tin in the deionized water will not precipitate through the previous system, and a new waste treatment process had to be developed. This system has an additional pre-treatment step that breaks the chemical bond between the stannous tin and the complexing agent prior to precipitation.

Results

After a year and a half in production, KEMET's new tin bath has realized all of the expected benefits. The complexing agents have extended the life of the bath from 2 weeks to more than a year and a half. Low surface insulation resistance is no longer a problem (Figure 2). The ability to analyze and control the organic additives makes bath performance predictable (Figure 3), and the higher pH electrolyte does not attack the newer dielectric formations. KEMET is ready to pursue greater productivity and smaller case sizes as surface-mount technology continues to advance the capability of ceramic chip capacitors.

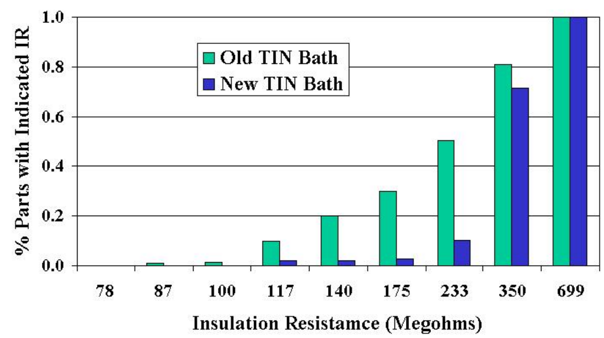

Figure 2. Insulation Resistance versus Tin Electrolyte

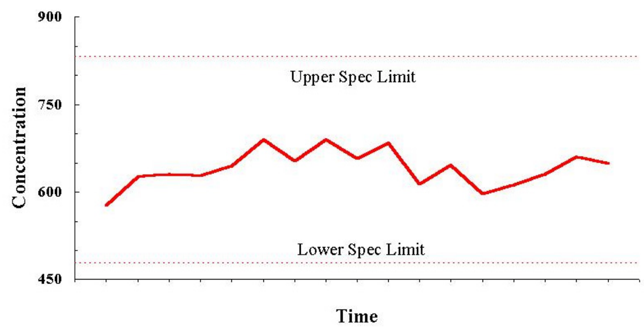

Figure 3. Organic Additive Concentration versus Time