Advice & Counsel

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Tin Basics

Dear Advice & Counsel,

While I have had some experience with acid tin plating solutions, I just was hired by a job shop doing alkaline tin plating. Can you give me the basics, so I can get up to speed fast?

Signed, Tin Man

Dear Tin Man,

The following information on alkaline tin plating has been gleaned from numerous literature sources over the years. Here goes:

The Basics

Tin is a very soft, conductive metal with a relatively low level of specific resistance.

Tin has a relatively low melting point. When applied over parts that are intended for use at high temperatures, tin can diffuse into base materials such as copper and brass. If the parts are stressed, a phenomenon called "liquid metal embrittlement" can cause stress fracture. For this reason, tin coatings are not recommended for fasteners made of steel, copper, copper alloys, aluminum, magnesium or titanium, and for serving at high temperatures, such as those that might be encountered in an automotive engine compartment (350ºF).

Tin can exist in two crystal structures, β or body centered tetragonal, and α, a cubic structure. Above about 13ºC (55°F), tin exists in the tetragonal β crystal structure and the metal has a density of 7.29 g/cm^3. Below 13ºC, the tin may undergo a transformation to the α form that is essentially non–metallic and much less dense (5.73 g/cm^3). This form of tin may be called alpha-tin, gray-tin or "tin-pest."

The initiation of this transformation is very slow to begin, so it is rare to encounter alpha tin, even when it is exposed at, and somewhat below, 13ºC, but at much lower temperatures (~ -40ºC) and over prolonged exposure at very low temperatures, once the transformation begins, alpha-tin may be visible within a few hours (see photo). This tin is dark, powdery, non-conductive and non-adherent.

The formation of tin pest can be eliminated by plating an alloy containing 0.2-0.3% bismuth, antimony or thallium.

Because tin is non-toxic, inert to many foods, and is easy to solder, it has widespread use in the food storage and food processing industry. In addition, tin deposits are used in various household appliances. Such deposits are also used extensively for coating wire products and for bearing surfaces, as well as in a variety of electronic applications.

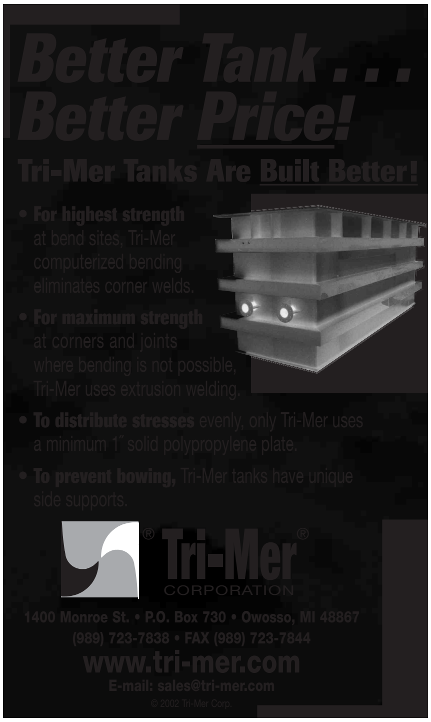
Generally, tin is employed due to its excellent ductility, resistance to corrosion and solderability. The majority of tin consumed is used for coating steel to enhance corrosion resistance and provide solderability. In electronic applications, tin deposits are used to enhance solderability and as an etch resist during the manufacture of printed wiring boards, and for the prevention of base metal tarnishing. Tin is widely used in electronic applications, including but not limited to: components, printed circuit board coatings, semiconductor devices, connectors, etch resist during printed wiring board manufacture, etc. Pure tin coatings from plating solutions containing additives such as brighteners are prone to whisker growth. Tin deposits from alkaline solutions do not have this problem. Tin whiskers can be prevented by plating a small percentage (0.3-1.0%) of bismuth with the tin.

Tin is used for food processing and shipping containers (*e.g.* "tin" cans), bearing surfaces, piping, wire coating, etc., to name a few applications. In addition, tin alloyed with other metals such as antimony, zinc, or copper, is used to form deposited alloys that have certain desirable chemical, electrical, and/or mechanical properties for specific applications. Lead and tin-lead plating are no longer in favor because of the toxicity of lead and because the European Union (EU) has banned the importation of lead containing coatings and products used in automotive and electronic applications.

An old term relating to tin plating thickness on steel sheet is a "base box." This is 112 sheets of steel, with dimensions of 20 in. x 14 in. = 31,360 in.^{2} of sheet or 62,720 in.^{2} of total surface area. Tin plating thickness is then referenced by pounds per base-box. 0.0001 in. (2.5 m) = 1.625 pounds/base-box, for example.

Alkaline Tin Plating Solutions

Most commercial alkaline tin plating solutions are formulated with potassium salts.



Potassium solutions deliver higher plating efficiencies at all normal operating temperatures vs. sodium based solutions. The drop in cathode current efficiency as the current density is increased is confirmation that these solutions will deliver excellent throwing power, allowing for more uniform deposits over complex shapes. Experience has shown that higher alkalinity content (caustic and carbonate) favor higher throwing power.

Stannate Salts

The stannate salts are part of the formulation in order to provide soluble tetravalent tin ions for reduction at the cathode. Variations in the concentration typically do not have a great effect on the operational characteristics of the solution. For normal plating current density range of 30–50 A/ft^2, a typical tin concentration is 42 g/L or about 5.5 oz/gal.

For plating at higher current densities, the concentration of tin is typically increased to as much as 300 g/L, at which current densities as high as 500 A/ft^2 may be employed. For these solutions, the potassium formulation is a must.

Commercial versions of stannate salts typically contain moisture, alkali, and carbonate, so the yield of tin may not be the theoretical percentages. Potassium stannate contains about 38.5% tin.

Alkali

The sodium or potassium hydroxide (1–3 oz/gal) is more important to control than the tin content, as it has a multitude of functions, including providing the conductivity of the solution, anode corrosion, and stabilizing the solution against hydrolysis of the tin or formation of stannite by reaction with carbon dioxide. For barrel plating, higher concentrations of alkali are typically required than for rack plating.

The free alkali content of the plating solution is critical to successful plating from this solution. It should be analyzed and adjusted daily, even if the solution is not in use, as alkali may be consumed by reaction with carbon dioxide in the air. Idle tanks should be covered with a lid or plastic sheeting. The free alkali can be lowered by the addition of 10% volume acetic acid. Acetic acid lowers free potassium hydroxide in a weight ratio that is close to 1:1.

Operation

The current density range is typically 30–100A/ft^2 for non-barrel plating and depends heavily upon the level of agitation, temperature and alkali content. Excess current density may produce nodules or rough deposits in the absence of adequate agitation or too low a temperature. Operational voltage tends to be in the 4–6 volt range, while barrel plating may require as much as 12 volts.

The operational temperature should be a minimum of 140°F (60°C). The high end of the range is not critical. At too low a temperature, the solution drops off dramatically in cathode efficiency, and rough deposits may be obtained. Normal cathode current efficiency is 60–90%.

Operating stannate tin plating solutions are typically straw color or cloudy and tend to generate sludge as they age. This sludge tends to be slimy and colloidal, making filtration a difficult proposition. Most platers allow the sludge to settle and remove it during annual tank maintenance. Sludge production is reduced when de-ionized water is used instead of tap-water. This sludge contains a significant amount of tin. Large facilities may use reclaimers to regain lost value from the sludge.

The stannate tin solution can tolerate high concentrations of carbonate without major operational problems. The carbonate is typically allowed to reach equilibrium with the drag-out rate. The solution is also very tolerant of heavy metal impurities, with the exception of antimony, which can cause a streaky deposit in low current density areas. Low current density dummying may remove it below harmful concentrations.

Stannous tin (stannite) is a contaminant in a stannate solution. It can break down to produce sludge by forming colloidal tin. The presence of stannite may also produce rough, spongy deposits.

A spot test for detecting this ion can be performed whenever stannite is suspected to be present.

Prepare the spot test solution by dissolving 5 grams of bismuth oxide or carbonate in 100 mL of 25% vol. hydrochloric acid. Add sodium hydroxide until the solution is alkaline, and then dilute to 250 mL. Add 10 mL of the hot (180ºF) plating solution to 5 mL of the spot solution. Production of dark precipitate is an indication of the presence of stannite.

To convert stannite back to stannate, dilute a small amount of hydrogen peroxide with water to make a 10% solution. Add this to the plating tank with a lot of agitation. After addition of the peroxide, the plating solution will need to be dummied until the excess peroxide is converted to water.

Anodes

It is important that the anodes dissolve as stannate (quadravalent) ions. Proper anode filming can be achieved by using dummy parts and raising the anode current density (voltage) until the voltage increases very rapidly and the anode develops a yellow-green film. At this stage the anode begins to dissolve as the stannate ion. After the yellow-green film forms on the anode, the current density should then be lowered to about 80 percent of the maximum value and operated in this range (along the “final curve” in the above diagram). The yellow-green color must be maintained for the anode to operate properly.

Too low an anode current density will result in the development of a gray color film, indicating that stannite tin is dissolving. Increasing the anode current density beyond that needed to generate the yellow-green color or not turning the voltage back to 80% of that which produced the green film will turn the film black, thus passivating the anode and causing no tin to dissolve.

An alternate method of anode filming is to remove all anodes and load the tank with dummies. Apply a voltage that yields twice the normal plating current and introduce the anodes one by one until all the anodes have been filmed. Then reduce the voltage to yield the normal plating current density, and replace the dummies one by one with parts. To maintain proper anode current density, partial tank loads must be avoided and in the case of automated plating equipment, dummies may need to be plated until a full load is present in the tank. ***P&SF***