Controlling Carbonate Buildup in Alkaline and Cyanide-based Plating Solutions through Continuous On-line Crystallization.

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Excessive carbonate concentration in alkaline and cyanide plating solutions through cyanide hydrolysis and anodic oxidation adversely affects plating efficiency. The conventional practice of controlling carbonates within acceptable limits was to batch treat these plating solutions by pumping them either into separate chiller tanks or into vessels placed outside of the plating shop during the winter. This paper takes a look at some of the previously accepted practices and compares crystallization with other alternatives.

Sodium carbonate is an essential component in sodium cyanide based plating solutions, as well as in many non-cyanide alkaline electrolytes, such as straight zinc and some zinc alloy formulations.

In freshly prepared plating solutions, the sodium carbonate content is normally around 30 - 40 g/l (4 - 5 oz/gal). At this level, carbonates increase electrical conductivity and help to buffer the solution pH. During normal operation, there is a gradual build-up of carbonates due to the decomposition of cyanide through anodic oxidation and by adsorption of the atmospheric carbon dioxide. Air agitation will enhance the formation of carbonates, as will a high anode current density, such as occurs in alkaline zinc baths when the anode area is reduced to control the dissolution of zinc metal.

Once the carbonate level rises above 60 g/l (8 oz/gal), adverse effects begin to occur which worsen as the concentration increases. Among the typical plating problems are: decreased throwing power and lower current efficiency with the corresponding dark deposits in recesses, lower brightness and higher brightener consumption, and reduced plating quality after bright-dipping. The effects of carbonate build-up are generally worse in rack plating than in barrel plating, since the carbonate concentration will be curtailed, due to the higher solution dragout with barrels.

Among the methods used to control excessive carbonate build-up are: dilution, solution replacement, precipitation with barium or calcium salts, freezing out, and ion exchange. While all of these methods rely on different mechanisms, they have certain elements in common: they all produce waste, plus other undesirable side-effects. With today's awareness and emphasis on waste minimization and prevention, the dilution option is virtually ruled out. The ion exchange route is a complex one, which has been adequately covered and detailed in a paper[1] presented at last year's AEFS/EPA conference for Pollution Prevention and Control.

For sodium-based electrolytes, freezing out seems a practical and cost-effective option. In colder climates, the conventional way was to pump out the solution into an outside storage tank during winter, and return it after the sodium carbonate had crystallized out. Apart from the downtime and the manual labor required, there were the unavoidable environmental and health hazards associated with the handling of cyanide solutions. Some platers also use home-made refrigeration units with cooling coils to achieve crystallization, but this method also requires a prolonged equipment shutdown. Freezing-out will not work with potassium-based electrolytes, due to the much higher solubility of potassium carbonate.

An innovative idea was presented by a Swiss inventor,[2] who developed a crystallizer[3] which connects straight onto the plating tank. This on-line system draws a small volume of 70 liters (18 gal) from the bath and cools it down to a preselected temperature, usually around 2 - 6 °C (35 - 42 °F). Once crystallization occurs, the solution empties onto a built-in moving belt filter, which retains the carbonate crystals for subsequent discharge into an existing waste treatment system. The treated solution is automatically returned into the plating tank, as the next batch is withdrawn for treatment. One full cycle takes approximately 60 - 80 minutes to be completed, so that 18 - 20 cycles can be performed in 24 hours. The yield per cycle varies according to the carbonate concentration in the feed stream, but it is typically around 5 - 6 kg (12 lb.) per batch.

Since the system operates fully automatic (except for having to remove the accumulated carbonate crystals from a storage bin), one crystallizer can be rotated among several plating baths in one shop. The collected crystals are so well drained of excess solution, that only traces of cyanide remain (one facility[4] reports <0.02 mg CN/kg). However, for safety reasons it is always recommended that these crystals be disposed of into the cyanide treatment section of an existing effluent treatment plant.

Regular carbonate removal ensures consistent plating quality and improved current efficiency. Because it generates so little waste and needs minimum labor, this method of crystallization is much safer and more environmentally friendly than other options. The smaller quantities of crystals are much easier to handle than one large quantity from an entire tank, such as occurs when the entire tank is treated at once.

One Midwest plating shop reported that they were able to improve plating efficiency by controlling the carbonate build-up, thus enabling them to meet increased production demands without having to install additional plating capacity. From all the available options for carbonate removal, this semi-continuous batch treatment crystallizer appears to meet the quality demands of a consistent finish in an uncomplicated and easy way, and without producing a negative environmental impact.

Summary

The adverse effects of excessive carbonate build-up in both cyanide and non-cyanide plating solutions are well known to platers, and they are adequately documented in the trade literature. Since this build-up occurs as a natural side-effect of the normal plating process, little can be done to avoid it.

As an option for controlling the carbonate concentration, this new sophisticated variation of the freeze-out technique appears to be very favorable, since it is continuous and generates a minimum of undesirable co-pollutants.

References

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[1] M.C. Reimer, Proc. AESF/EPA 17th Annual Conf. p.113 - 117; (1995).

[2] R. Leutwyler, U.S. Patent No. 19920115

[3] CARBOLUX, JWI, Inc., Holland, MI.

[4] New Brunswick Plating, New Brunswick, NJ.