Is Cadmium Finished? (Continued)

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We continue our discussion of cadmium plating from last month:

Anodes

Cadmium anodes are almost always chill cast, containing 99.9% cadmium, with silver + lead + tin at 0.05% maximum, arsenic + thallium at 0.005% maximum. Balls placed into spiral steel wire baskets or in titanium baskets typically serve as the plating anodes. Steel, or carburized steel, can be used as insoluble anodes to reduce high levels of cadmium from the solution (but some iron cyanide will be produced as a result). The maximum anode current density in most applications is about 20 A/ft^2 (2 A/dm^2).

When using steel baskets, the entire basket needs to be kept full at all times. In the above photo, it is clear that by not keeping the anode baskets full, the basket wire has been dissolved over time, as the wire is thinner at the top than further below the plating solution. While this is not a major mistake, it does produce iron cyanides, which reduce the plating solution efficiency and can impact both salt spray performance and hydrogen embrittlement effects.

Polarized anodes can be caused by operation at excessively high current densities, chromate contamination or nitrate contamination. Well working cadmium anodes typically are gray in color. A powdery black or burnished appearance indicates that the anode is polarized. A polarized anode produces oxygen through decomposition of hydroxide ions. The end result is a drop in metal, free cyanide and hydroxide concentration over time. The carbonate content will increase. However, since the oxygen overvoltage potential on steel is significantly higher than on cadmium, it is nearly impossible to completely polarize the cadmium anode balls placed into steel anode baskets. Any cyanide solution that is used with steel anode baskets or bare steel tank walls will produce rapid corrosion of the steel, if contaminated with chloride.

Operating conditions for rack plating

If used, cadmium brighteners are temperature sensitive, causing a dull deposit if the temperature goes much above 85 to 90°F (29 to 32°C) or below 70 to 75°F (21 to 24°C). Also, as the temperature is increased, the throwing power of the solution is reduced, while the plating speed and the grain size of the deposited metal are increased. For rack plating, the sodium hydroxide is typically limited to that which is naturally produced at the cathode. Excess sodium hydroxide causes a narrowing of the bright range. Higher concentrations of cadmium may tolerate more sodium hydroxide without suffering this effect.

The usable cathode current density varies with the concentration of cadmium metal, ratio of total cyanide to metal, temperature and level/type of agitation. Under typical temperature and agitation conditions, the maximum cathode current density is about 20 A/ft^2 with a cadmium metal content of 3.0 oz/gal (22 g/L) and 40 A/ft^2 with the cadmium content at about 5.5 oz/gal (41 g/L). Excessive cathode current density can result in dull, porous deposits, anode polarization and solution compositional changes (The NaOH content will go up.).

Cathode current efficiency is typically greater than 90% and may be as high as 98% when the metal content is relatively high, and temperature and agitation are on the high end of the acceptable ranges. Efficiency tends to drop with higher free cyanide, lower temperatures, lower levels of agitation and higher sodium hydroxide content. Carbonate concentrations over 8 oz/gal (60 g/L) will also drop cathode current efficiency.

The minimum anode to cathode area ratio is 3:1, which is easy to exceed/maintain with anode baskets.

Operating conditions for barrel plating

The plating voltages for small barrels (less than 14” diameter × 30”) typically is 6 to 8 V while larger barrels may require up to 12 V_{DC}.

The solution used for barrel cadmium plating is typically lower in cadmium content than for rack operations (high cyanide to metal ratio). Current densities are much lower than for rack plating (5 to 7 A/ft^2), and may vary a small amount based upon the metal concentration, sodium hydroxide concentration and operating temperature.

Aside from the ratio of total cyanide to cadmium, it is important to maintain a minimum hydroxide concentration to maintain part-to-part-uniformity of plating thickness.

Complicated shapes may require the use of ballast to assure that contact is made with all surfaces to be plated.

Hydrogen effects

Although highly efficient, cadmium solutions produce some traces of hydrogen during plating, enough to cause hydrogen embrittlement failures. Hydrogen embrittlement failures occur catastrophically during or some time after part loading. The higher the hardness or tensile strength of the steel, the more sensitive it is to this problem. Parts with tensile strengths above 200,000 psi (1,380 MPa) or a hardness above R_C43 should not be electroplated with cadmium, according to QQP-416.

Relieving hydrogen embrittlement involves baking at high temperatures to reduce the hydrogen content of the steel and redistribute the remainder of the hydrogen throughout the steel to reduce local concentrations at imperfections in the steel structure. For this reason, brighteners should not be used, as brighteners cause the cadmium to be less porous, making removal of the hydrogen at the steel-cadmium interface more difficult.

Hydrogen failures are caused by diffusion of absorbed hydrogen ions to imperfections in the steel. Once the hydrogen has diffused to these imperfections, it is very difficult to remove and redistribute the hydrogen, resulting in failures. Therefore parts should be treated by baking as soon as possible after plating. Many specifications require baking within 4 hours after plating, and some have been changed to require baking within one hour after plating.

Treating for hydrogen

While it is highly desirable to bake plated parts at temperatures above 375°F (191°C), parts that can not tolerate such high temperatures can be baked at 275°F (135°C), but for an extended periods of time, usually 23 hours minimum. These parts should also be stress relieved prior to plating. By analogy, if parts can withstand higher temperatures, hydrogen relief baking can be made more effective by increasing the temperature. Aerospace parts made of 17-4 PH steel, for example, have been baked at 450°F (232°C) instead.

Specifications vary as to baking temperatures and times. In general, 375°F (191°C) is a commonly specified temperature, but baking times vary depending on the type of part and the experience level with that part in service. It is always safest to bake for 23 to 24 hours. Baking beyond 24 hours has not been shown to provide any additional benefit. The thicker the plated deposit, the longer the bake should be. While there is some disagreement with the hardness level that requires a bake, in general it is understood that parts above R_C36 require baking. Parts between R_C34 and 35 require stress relief prior to plating, and parts below R_C34 require no baking or stress relief. However, always follow the specified procedure for any given part.

Cadmium plating problems

Pitting

While rarely encountered in barrel plating, pitting in rack plating operations may be a result of excessive current density, residuals from poor cleaning or thallium contamination from low grade anodes. Pitting caused by thallium contamination may be compensated for, by adding a surfactant such as castor oil or sodium alkyl aryl sulfonic acid. Small additions of dilute peroxide may also be beneficial by consuming hydrogen ions as they are formed on the plating surface, but this should be a last resort.

Metallic contamination

Cadmium plating solutions are highly sensitive to a number of trace metal impurities. The most troublesome are antimony, lead, arsenic, tin, silver and thallium. As in any cyanide process, hexavalent chromium contamination can cause skip plate or blisters. The typical effect of the other metallic contaminants is discoloration of the cadmium deposit, which sometimes is not visible until after chromate conversion coating. Cadmium deposits containing metallic impurities will yield lower salt spray performance due to the formation of galvanic cells.

Lead and silver contamination may be treated by precipitation with a sulfide-containing purifier, while hexavalent chromium contamination is treated by reducing the valence to the trivalent state by the addition of a reducing agent such as hydrosulfite or dextrose.

Cadmium is very tolerant to zinc and copper contamination (up to 1 oz/gal), but when these metals reach troublesome levels, there is no way to remove them. While the literature may recommend treatment of cadmium plating solutions that have been contaminated with copper and other more noble metals with zinc dust or cadmium "sponge," such treatments produce waste that may be highly flammable and therefore such treatments are not recommended. Mild cases of contamination may be treatable through low current density dummying at 2 A/ft^2 (0.2 A/dm^2) for 24 to 48 hours, although reported successes have been rare.

There is apparently no cure for copper and nickel contamination. Since copper contamination can result from cleaning of or drippage from tank bus-work, it is desirable to use titanium clad copper for tank bus instead. Nickel is typically not a problem until it attains a concentration exceeding 200 ppm, and at much lower concentrations, may be beneficial as a brightener. However, nickel contamination may aggravate hydrogen embrittlement problems, even at low concentrations, by producing a denser, less porous cadmium deposit.

Sulfide treatment

Since both cadmium and some metallic impurities can react with sulfide to precipitate insoluble cadmium sulfide solids, sulfide treatment must be performed with acceptance of some loss of cadmium from the treatment procedure. Losses can be minimized by carefully conducting Hull Cell experiments to confirm treatment success, and verify the amount of sulfide necessary. Excessively large additions of sulfide will result in dull milky-gray deposits. Any sulfide treatment may affect the appearance of the deposit after bright dipping.

The following is a treatment procedure described by Herbert Geduld (*Metat Finishing*, August 1964; page 52):

1. First plate an "As Is" panel, replicating the plating conditions as closely as possible.
2. If heavy metal contamination is suspected from dull in LCD areas, or gray to black condition at high current densities on the panel, add the equivalent of 0.01 oz/gal sodium sulfide or polysulfide to the test cell.
3. Repeat the test panel at original amperage and time. If beneficial effects, such as widening of bright range or complete elimination of gray streaks appear, add another increment of 0.01 oz/gal and repeat the test panel. Repeat as necessary.
4. From the test panels determine the optimum amount of sodium polysulfide to add to the bath without the formation of yellowish stained deposits at low current density areas.
5. Weigh or measure out this amount of sulfide for the total bath, dilute with large amounts of water *i.e.*, 2 to 3 gallons per ounce, and distribute uniformly throughout the bath with adequate stirring. If possible, this treatment should be followed by settling and filtration, since there is a slight tendency for the precipitate to redissolve over time.

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Cast iron

1. Soak clean.
2. Water rinse.
3. Anodic clean as above for HSLA steels.
4. Water rinse.
5. Pickle / condition, 60 g/L (8 oz/gal.) for 3 to 5 min.
   Note: Temperatures of 49 to 71°C (120 to 160°F) will speed the pickling action and remove red rust more quickly.
6. Water rinse.
7. Immerse in 0.5 vol% ammonium hydroxide for 30 sec. Omit this step for plating deposits other than electroless nickel.
8. Plate.
9. Rinse and dry.

Case-hardened steel

1. Anodic electroclean (reverse current).
2. Water rinse.
3. Pickle / condition, 30 vol%, 49°C (120°F) for 2 min.
4. Water rinse.
5. Immerse in 0.5 vol% ammonium hydroxide. Omit this step for plating deposits other than electroless nickel.
6. Plate.
7. Rinse and dry.

Leaded steel (free-machining steels) or leaded brass

1. Soak clean.
2. Water rinse.
3. Cathodic clean (direct current) followed by 15 to 30 sec anodic in separate solutions.
4. Water rinse.
5. Pickle / condition, 60 g/L (8 oz/gal) at ambient temperature for 3 min.
6. Water rinse.
7. Immerse in 0.5 vol% ammonium hydroxide for 30 sec. Omit this step for plating deposits other than electroless nickel.
8. Plate.
   Note: For leaded brass a copper strike is recommended before nickel plating to cover the lead in the surface. The nickel plating solution will form lead sulfate resulting in "stardusting".
9. Rinse and dry.

Nickel and nickel-plated deposits

1. Direct current (cathodic) electroclean for 1 min.
2. Water rinse.
3. Pickle / condition, 20 vol%, 49 to 54°C (120 to 130°F).
4. Water rinse.
5. Plate with electroless nickel or electroplated nickel.
   Note: This cycle can be used for bumper replate operations. Longer cleaning cycles to remove buffing compound are usually required for bumpers.

Leaded bronze

The cycle is the same as for case-hardened steel.

Kovar

Many process cycles for the activation of Kovar include alkaline permanganate and mineral acid steps. The pickle / conditioner solution is used to replace these steps. The pickle / conditioner is used at 15 vol%, 49°C (120°F) for 5 to 6 min.

Tarnished brass

1. Alkaline soak clean.
2. Water rinse.
3. Anodic (reverse current) electroclean for 20 sec at low current density.
4. Water rinse.
5. Pickle / condition, 20 vol%, 24°C (75°F). Use anodic (reverse) current, 6 V for 0.5 to 2.0 min.

Note: Portions of this column were presented at the EN '95 Conference, sponsored by *Products Finishing* magazine. P&SF

Answers to I.Q. Quiz #428

1. (d) uses no electrical current
2. The cold welding of fine metallic particles to the metal (usually steel) substrate
3. Glass beads, fine metal particles in suspension and parts are rotated in an oblique barrel. The impact energy imparted by the glass beads cold welds the metal fines to the substrate.
4. Zinc, tin, cadmium, other ductile metal and mixtures thereof
5. Hydrogen embrittlement and the requirement for post-plate baking are significantly reduced with cathodic hydrogen from electroplating. Hydrogen arising from cleaning and pickling is still a lesser factor.

Advice & Counsel

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Discolored cadmium plate

Dull and dark deposits may be caused by conditions other than metallic contamination, including organic breakdown products, high carbonate content, high DC ripple and low metal content. Geduld reported a temporarily dull deposit caused by adding too much caustic over too short a time period (more than 0.5 oz/gal over 8 hours). No explanation for this was provided.

Organic contamination from additive breakdown products and other organics that may have been brought into the solution via drag-in can be removed by carbon treatment or carbon filtration.

Cyanide cadmium plating solutions are exceptionally sensitive to carbonate content and require more frequent carbonate removal than other cyanide-based solutions. High carbonate content can cause a narrowing of the bright range and dark streaky deposits. Very high concentrations can cause anode polarization and roughness.

Cadmium plating solutions are also sensitive to rectifier ripple. Ripple greater than about 5% can result in dull deposits or a shift in the bright range to the higher current density ranges. Even if a tap switch rectifier is in good shape, it can produce unacceptable ripple if the taps are improperly set (notches between taps exceeding 1).

Low cadmium metal content typically results in a hazy deposit at low current densities and may yield burning at high current densities in rack plating operations.

If a cadmium deposit is bright immediately after plating, but dulls up or yellows after bright dipping in a chromic acid based bright dip, the following possible causes are noted in the literature:

1. The bright dip is contaminated with copper, nickel or other heavy metals.
2. The rinse ahead of the bright dip is contaminated with heavy metals.
3. The cadmium plating solution is contaminated with heavy metals

Immersion in a dilute nitric acid solution ahead of the chromate can reduce the tendency for discoloration in the chromate.

More next month ….. P&SF