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Is Cadmium Finished?

Dear Advice & Counsel,
I work at a large aerospace firm on the east coast. I've recently been transferred to the finishing department. I have a background in zinc plating, but I have to admit that I thought cadmium plating was dead as a doornail, until I got here. We do cyanide cadmium, Ti-cad and cadmium-nickel diffused. I can find a lot of information on the first and almost nothing about the last two. Why are these processes still being done, and can you provide information on all of them for me?

Signed,
Vlad the Cad

Dear Vlad,

We can start with the issue of cadmium plating:

Cadmium has toxic properties and cadmium salts have been linked to cancer, making this metal a pariah in the electroplating field. The number of sources for cadmium plating has trickled down to just a few, but those that are left are pretty busy meeting customer demand. As you probably already know, cadmium is heavily regulated by the EPA and OSHA, and is one of the "banned" materials in the European ELV and RoHS Directives. However, none of these limitations prevent cadmium and associated finishes from being applied in aerospace, military and non-ELV/RoHS applications.

We begin by looking at the metal's properties. Cadmium is a soft, white metal that offers excellent lubricity. Lubricity is a property that allows parts that are plated with cadmium to be disassembled after a period of service without significant damage to the surface finish, even if corrosion has occurred. This is very important in the aerospace industry, as jet aircraft components are periodically taken apart and put back together again. Cadmium is easily soldered, even after significant storage (using a mildly activating rosin flux). It offers a high level of corrosion protection for ferrous substrates in chloride (sea salt) environments, as cadmium sets up a sacrificial galvanic cell with iron under such conditions. In sulfate (*e.g.*, acid rain) environments, cadmium tends to become the cathode in a corrosion cell with iron, thereby not providing sacrificial protection in such environments. It has a relatively low melting point, making pure cadmium coatings unsuitable for switching applications (but a much higher melting alloy of cadmium and silver can be used in such applications). Cadmium produces a favorable galvanic couple with aluminum, while other corrosion protective coatings may cause the aluminum to corrode. A typical application that takes advantage of this property is cadmium-plated steel rivets for assembling aluminum truck trailer components. Cadmium produces low-volume corrosion products that tend to adhere to the plated surface (vs. zinc which produces high volume corrosion products that spall off).

The toxicity of cadmium can actually be an advantage, as fungus and mold do not grow on a cadmium plated surface. Substitutes for cadmium that may be considered include zinc-nickel, zinc-cobalt, zinc-iron and tin-zinc alloy plated deposits. While each of these may provide some of the benefits of cadmium, no one substitute offers all of the above features.

Commercial cadmium plating dates back to the beginning of the 20th century. While cadmium plating has declined as a prescribed finish over the past years, it is still an important electroplated coating that continues to be employed in special applications where specific properties can be taken advantage of.

Electroplated cadmium can be bright or dull and typically requires a relatively thin deposit for protection against corrosion as well as a base for painting (after chromating). The aerospace industry typically specifies dull, porous cadmium plating, as this finish is easiest to treat for hydrogen embrittlement (also known as hydrogen stress cracking) relief. When hydrogen effects are not important, and a bright finish is desirable, cadmium can be deposited from solutions containing additives for a fully bright silvery-white appearance.

While there are numerous corporate specifications for cadmium plating, those most often referenced are QQP416 and ASTM B766.

There are applications where cadmium plating should not be employed. For example, QQP416 warns that cadmium plating should not be used on titanium parts or parts that are to be mated with titanium components. Parts that have been hardened beyond Rockwell C50 should not be cadmium plated, as they may be hydrogen-embrittled during plating to a degree that can not be "cured" by baking.

Because it is poisonous, cadmium plating should not be employed on any parts that will touch any portion of the food chain.

Equipment for cadmium plating

The plating tank can be bare steel, but to avoid formation of difficult to waste-treat iron cyanides, a hard PVC-lined or a polypropylene tank should be used. The tank should be equipped with an overflow dam as shown in Fig. 1, to eliminate any floating debris or oil. A liquid level sensor may be employed to warn of a leak and maintain the correct liquid level. Titanium heating/cooling coils are preferred over steel for the reason just discussed.

Continuous filtration with a two-tank turnover rate is highly desirable. A carbonate chiller or treatment tank for carbonate removal is also desirable. However, cadmium plating tanks that are operated at lower temperatures (60°F; 15°C, attained through use of a chilling coil) have been reported to form little or no excess carbonates.

Eductor agitation is preferred, as it produces a high degree of agitation without accelerating carbonate formation.

The tank shown in Fig. 1 is not ventilated. While cadmium plating solutions yield little or no emissions (as confirmed by air testing conducted by NIOSH in the 1980s), it is a good idea to vent the tanks from a safety standpoint, as accidental additions of acid by careless operators can release toxic cyanide gas.

Cadmium plating solutions

While cadmium can be plated from acidic solutions based on sulfate, chloride or fluoborate chemistries, the vast majority of cadmium plating and all Ti-cad and cadmium for cadmium-nickel diffused coatings is conducted from a cyanide formulation.

Cyanide-based cadmium plating solutions offer high throwing power and the ability to deposit a highly porous, dull deposit that is more easily treated for hydrogen embrittlement relief baking. The alternative solutions mainly offer the absence of cyanide, which can be a big advantage in certain parts of the U.S.

Shown in Fig. 2 are two formulations for cyanide-based cadmium plating. A key control factor is the ratio of the total cyanide-to-cadmium. Ratios as low as 2.8 can be found in the literature, but those shown are more common. Solutions with a low ratio tend to provide the best appearance and are typically used in bright cadmium plating.

Solutions with low ratios are used in plating high strength steel that is sensitive to hydrogen embrittlement because the solution plates at close to 100% cathode current efficiency (producing the least amount of hydrogen gas). However, these solutions have poor throwing/covering power and may deposit very little cadmium in deep recesses.

Solutions with a high ratio of total cyanide-to-cadmium content provide the most uniform coverage (known as throwing power). These formulations are typically employed when plating very complex shaped parts or in barrel plating. In such applications deposit appearance is secondary (not mirror bright but uniform in color and free from high current density burns).

Additives for cadmium plating solutions

With no additives, cadmium deposits are large-grained and very porous. Grain sizes ranging from 5 to 8 microns have been reported. This structure lends itself to the easiest for hydrogen embrittlement relief. Modern solutions are operated with no or low concentrations of additives in applications where hydrogen embrittlement is a possibility and for airline/aerospace or military applications. Some specifications dictate a fully dull, additive-free plating solution.

Brighteners are undesirable in applications requiring hydrogen embrittlement relief baking, because the deposit is too dense to allow for easy escape of some of the absorbed hydrogen. Studies [W. Paatsch & V.-D.Hodoroaba, *Plating & Surface Finishing*, **89** (10), 57 (2002)] have shown that only about 30% of the absorbed hydrogen ever leaves the part during baking. The other 60% is redistributed and locked up inside the steel crystal structure.

Additives for cyanide cadmium plating solutions were developed as early as 1925. These additives were initially proteins or protein derivatives. A common tale in the plating industry is the one of a researcher dropping his wool sweater into the plating "vat" and discovering the cadmium solution now plated bright. Another story told to me by Jack Hendricks (deceased) was that after he heard about the sweater, he started using all kinds of proteins in his search for a cadmium brightener and found that Postum Cereal® worked extremely well. According to Jack, in the 1930s, there was far more Postum Cereal® that went into cadmium plating tanks than into kid's tummys. Other brighteners for cadmium plating included sulfonic acid derivatives, nickel or cobalt, aromatic aldehydes and cellulose derivatives. All brighteners used today are proprietary products. If used, additive concentrations are typically controlled by routine Hull Cell tests.

Cadmium plating solution ingredients

Cadmium

The source of cadmium ions in a plating solution may be cadmium oxide or cadmium cyanide. While there is uncertainty as to the exact complex that is formed when cadmium oxide is reacted with sodium cyanide to produce the soluble complex, a simplified formula is $Na_2Cd(CN)_4$.

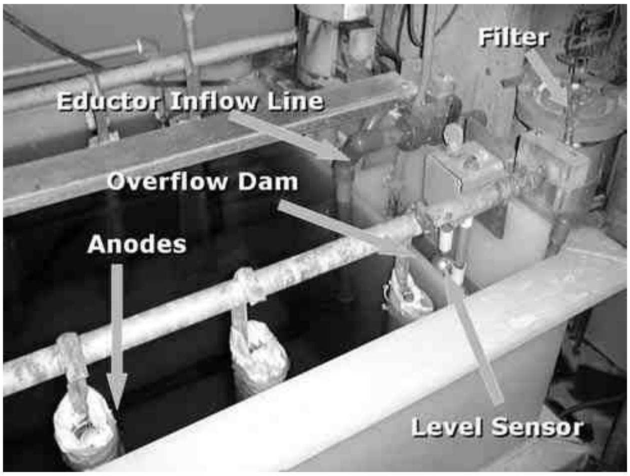
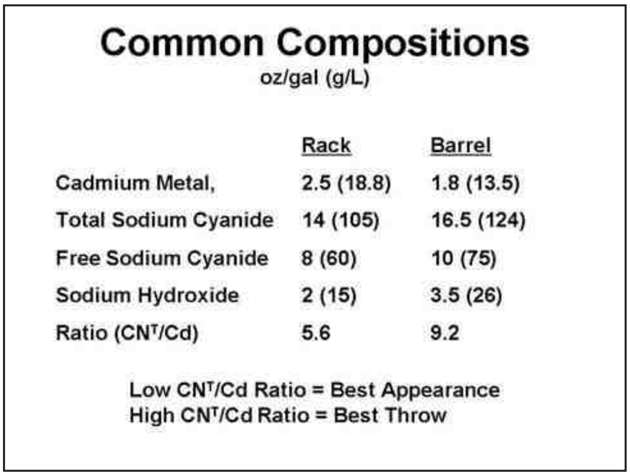


Figure 1.



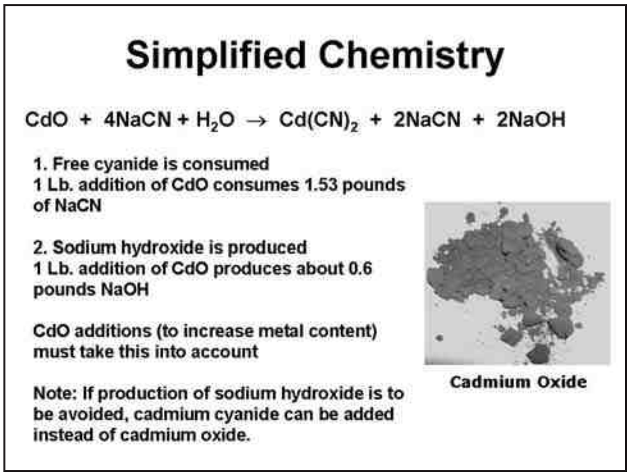
Common Compositions

oz/gal (g/L)

	Rack	Barrel
Cadmium Metal,	2.5 (18.8)	1.8 (13.5)
Total Sodium Cyanide	14 (105)	16.5 (124)
Free Sodium Cyanide	8 (60)	10 (75)
Sodium Hydroxide	2 (15)	3.5 (26)
Ratio (CN^T/Cd)	5.6	9.2

Low CN^T/Cd Ratio = Best Appearance
High CN^T/Cd Ratio = Best Throw

Figure 2.



Simplified Chemistry

$CdO + 4NaCN + H_2O \rightarrow Cd(CN)_2 + 2NaCN + 2NaOH$

1. Free cyanide is consumed
1 Lb. addition of CdO consumes 1.53 pounds of NaCN

2. Sodium hydroxide is produced
1 Lb. addition of CdO produces about 0.6 pounds NaOH

CdO additions (to increase metal content) must take this into account

Note: If production of sodium hydroxide is to be avoided, cadmium cyanide can be added instead of cadmium oxide.

Figure 3.

Figure 4.

While the cadmium is bivalent (+2), the complex ion involved in deposition has a -2 valence. This negative valence lends itself to high throwing power by limiting the population of cadmium ions available for deposition in the boundary layer where deposition occurs. This makes agitation an important variable to control.

Cyanide

Any cyanide present in the solution beyond that required to produce the complex is called "free cyanide." Since free cyanide in cadmium solutions may be difficult to analyze reliably, many platers chose to control the bath by monitoring the total sodium cyanide (free plus complexed) and/or the ratio of total sodium cyanide to cadmium. The free cyanide produces some conductivity, but is mostly important to proper anode corrosion. For analytical control purposes, the total cyanide or the ratio of the total cyanide to the cadmium is set and controlled.

Shown in Fig. 3 is a basic chemical reaction between cadmium oxide and sodium cyanide to produce soluble cadmium cyanide. While this equation may not be wholly accurate, it is shown to emphasize that each time cadmium oxide is added to a plating solution, it will impact the concentration of two other ingredients:

1. The free cyanide will be reduced as sodium cyanide is consumed by the reaction. For each pound of cadmium oxide added to the solution, 1.53 pounds of sodium cyanide must be added to avoid reducing the free cyanide content.
2. Sodium hydroxide will be produced (concentration will increase). For each pound of cadmium oxide added to the solution, about 0.6 pounds of sodium hydroxide is produced. If production of sodium hydroxide is to be avoided, cadmium cyanide can be added instead of cadmium oxide.

Since the performance of the plating solution is directly tied to the concentrations of free cyanide and sodium hydroxide, cadmium oxide additions must take into account.

Sodium hydroxide

Sodium hydroxide may be intentionally added, or it will be produced at the cathode due to the difference in anode current efficiency vs. cathode current efficiency of the solution. Sodium hydroxide increases the conductivity of the solution significantly, which makes it desirable in barrel plating applications. Excessive concentrations of sodium hydroxide (sometimes caused by plating at current densities that yield a disparity between anode and cathode efficiency) can reduce the bright plating current density range, so additions must be made with care to confirm a beneficial effect. Hull Cell tests can be conducted to assure that the bright range will not be impacted by an addition of sodium hydroxide.

Carbonates

Carbonates are considered an impurity in cadmium plating solutions and should be controlled to less than 8 oz/gal (60 g/L). Excessive carbonates can result in higher plating voltages, lower bright range, lower plating efficiency (more hydrogen gas generation) and at high concentrations, roughness due to precipitation of carbonate crystals. The deposit may also exhibit a lower level of ductility due to the deposition of larger grains.

The maximum tolerable concentration of carbonate depends on the solution operating temperature and the cadmium metal content. Higher temperatures and lower metal concentrations amplify the bad effects of carbonate. A typical maximum solubility of sodium carbonate is around 14 oz/gal (~100 g/L). Carbonates can be removed by reducing the temperature to near freezing or by chemical precipitation using barium salts such as barium nitrate. The freezing method is preferred. Shown in Fig. 4 is a small freezer chest used by a client to separate carbonates from his cadmium plating solution. A stainless steel rod acts as a seeding source.

More next month … ***P&SF***