

# Alternatives to Cadmium Coatings For Electrical/Electronic Applications

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Although cadmium is widely used because of its unique properties, it's on the "hit list" as one of 17 chemicals in the Industrial Toxics Project of the U.S. Environmental Protection Agency (U.S. EPA) for voluntary use reduction. A survey is provided of candidate alternative coatings systems, with emphasis on nickel, tin and zinc alloys. Because the properties of some of these candidate coatings compare favorably with cadmium, this information should be of use to those who have to find replacements for cadmium.

Cadmium is widely used in engineering applications because of its unique properties. The coatings are adherent, smooth and ductile, and may be applied to a wide range of metals. For electrical and electronic applications, which make up about one-quarter of the market for cadmium coatings, ease of solderability and high electrical and thermal conductivity, along with low contact resistance, are important properties. In addition, if corrosion does occur, the corrosion products are not voluminous and do not cause the types of problems seen with zinc coatings, for example.<sup>1</sup>

When these characteristics are coupled with the good lubricity (low coefficient of friction) cadmium exhibits, it is not surprising to find cadmium coatings used for switches, contacts, sockets, relays and connectors, as well as bonding surfaces. Table 1 lists some of the applications of cadmium (and cadmium compounds) in the electrical/electronic products industry. Table 2 describes types of cadmium Coatings according to Federal Specification QQ-P-416. Cadmium is typically plated on ferrous substrates, but is sometimes used on nonferrous substrates, such as aluminum or titanium alloys.

## Environmental Concerns

The Occupation Safety and Health Administration (OSHA) has set very low limits for worker exposure to cadmium. In addition, cadmium (including its compounds) is one of 17 chemicals

Application	Component
Motors	Brushes, commutators, slip rings
Batteries	Electrodes for nickel-cadmium and mercury-cadmium cells reference cells
Battery packs	Holders contacts, sockets, connectors, bonding surfaces
Printed circuit boards	Solder (fatigue resistant), bipolar transistors holders, connectors
Cabinets, housings	Latches, hinges, fasteners, chasses, EMI shielding
Switches, relays	Contacts
Photovoltaic cells	Semiconducting materials, contacts

targeted by the U.S. EPA for voluntary reduction. The goals are a 33 percent reduction in cadmium releases to the environment for 1992, and 50 percent by 1995. The baseline for these reductions is the data from the 1988 Toxic Release Inventory (TRI):<sup>2</sup>

To compound the finishers' problem, about 90 percent of cadmium coatings are applied by electrodeposition, usually from a cyanide-based plating bath. Cyanide is a reactive compound that can generate atoxic compound if not handled properly. It's also included on the hit list of 17 chemicals.

Another dimension to the problem can be seen upon inspection of Table 2, which shows that for improved corrosion resistance in aggressive environments, a chromate coating is specified, meaning that an additional toxic metal (chromium) has to be treated before discharge.

The U.S. government, particularly the Department of Defense, has identified cadmium plating as an environmentally unacceptable process, and has funded

programs to find substitutes. The Defense Construction Supply Center has funded one study,<sup>3</sup> while the Defense Electronics Supply Center plans to reduce or eliminate cadmium under its Hazardous Materials Minimization Plan. In Europe and Scandinavia, several countries have passed legislation restricting the import or export of cadmium-containing products. The European Economic Community (EEC) has passed Council Directive 91/338/EEC, which prohibits the use of cadmium-plated products by June 30, 1995.<sup>4</sup>

Industry is also taking a more aggressive role in reducing the use of

Classification	Description
Type I	As plated deposit
Type II	As plated plus chromate coating
Type III	As plated plus phosphate coating
Class 1	0.0005 inch thick deposit
Class 2	0.0003 inch thick deposit
Class 3	0.0002 inch thick deposit

NOTE: Type II, Class 2 will provide a corrosion resistance of 96 hr, minimum in the ASTM B-117 salt spray test.

**Table 3**  
**Candidate Substitute Coatings for Cadmium**  
**As Published in the Literature**

Type of Coating	Candidate	References <sup>(a)</sup>
(1) Metals	Al	15,18,20,21,24,30,44,45
	Ag	44
	Ni	14,22,34
	Sn	5,6,7,11,12,19,37
	Zn	6,7,9,11,12,13,17,21,24,54
(2) Alloys	Ni-Co	33
	Ni-Fe	31,42,43
	Ni-P	14,22,27,28,29,32,36,38
	Ni-Zn	(See Zn-Ni)
	Sn-Co	19
	Sn-In	16
	Sn-Pb	7,19,34,37
	Sn-Ni	19,46,48
	Sn-Pd	26
	Sn-Zn	5,7,16,19,35,37,41,47
	Zn-Al	21,50,51
	Zn-Co	24,50
	Zn-Fe	24,50
	Zn-Mn	24,50
	Zn-Ni	10,18,24,25,40,41,55
(3) Mixtures	Ni + BN, PTFE, SiC, SiN or diamond	27,38,39
	Ag + SnO <sub>2</sub>	8
	Sn + Zn	5
	Zn + Al	21
	Zn + SiO <sub>2</sub>	49
(4) Compounds	TiN	44,54
	Silicates	23

(a) Not a comprehensive listing; a few examples are listed when there is reference to electrical/electronic applications.

“end of pipe” solution. The problem is only controlled, not eliminated.)

2. Process modification, efficiency improvement. (The amount of toxic waste to be treated is reduced, but not eliminated.)

3. Materials substitution, partial or total. (Applied at the front-end of the process, where substitution can lead to partial or full elimination of the toxic waste problem.)

This paper is concerned only with the third approach. It should be emphasized, however, that because cadmium exhibits such a wide range of desirable properties, it may not be possible to find a suitable substitute for some applications. In these cases, the first and second approaches must be employed, preferably with a non-cyanide bath, or an alternative deposition technique such as mechanical plating, vacuum evaporation, ion plating or sputtering should be used.

#### Finding Substitute Coatings

Data from product bulletins, unclassified and non-proprietary reports, technical arti-

solutions. One commercial process has been available for a number of years,<sup>56</sup> and, more recently, a new bath has been developed<sup>6</sup> for the plating of lead frames. For some applications, especially aircraft components, an ion vapor deposition (IVD) process has been commercialized, and this is an acceptable substitute for cadmium in some military specifications.<sup>20</sup> IVD is a vacuum-based coating technique, however, that has difficulty coating inside tubes or deep recesses. Like mechanical plating and other commercial processes for aluminum, the deposits tend to be porous and only exhibit maximum corrosion protection after being given a chromate-type of conversion coating. The deposits are ductile and exhibit good adhesion. The fatigue properties are better than those of cadmium.

Aluminum does provide sacrificial protection—like cadmium—to ferrous substrates, and hydrogen embrittlement of the substrate is not a problem. The corrosion products are similar to those of cadmium, but the tribological properties are worse, and the aluminum coatings are much more difficult to solder because of the thin oxide film that forms on exposure to the atmosphere. Corrosion resistance in humid, acid or marine (chloride) environments is similar to that of cadmium, while it is more resistant in sulfur-containing atmospheres. Aluminum coatings can also be used at higher operating temperatures than cadmium coatings. Overall, however, aluminum does not appear to be a strong candidate for electrical/electronic applications.

#### Nickel

Nickel may be applied by electrolytic or electroless plating techniques. Nickel coatings are useful because they avoid the problem with “whisker” growth and electromigration found to some extent with cadmium or zinc coatings, and to a much greater extent with tin and silver coatings. Such coatings are relatively hard and do provide good wear and abrasion resistance.

Although they exhibit relatively good corrosion resistance, especially in alkaline environments, nickel coatings tarnish quite easily, especially in sulfur-containing environments. They provide corrosion protection by forming a physical barrier on the surface of the substrate. Nickel does not give sacrificial protection, like cadmium, and the degree of protection depends on the integrity of the coating and the aggressiveness of the environment. Nickel coatings perform worse than cadmium in marine, rural and

cadmium. Companies serving the aerospace industry and providing military hardware (Pratt & Whitney, Boeing) have active projects underway and are beginning to generate specifications for substitute coatings. Ford Motor Company has said it will sell only cadmium-free products by the 1995 model year. Caterpillar has a similar objective, except its target date was January 1993.

#### Reduction Options Available

There are three general approaches to toxic or hazardous waste reduction and/or elimination:

1. Waste treatment, recovery and recycling. (Sometimes referred to as an

cles, scientific papers and patents have been reviewed, with particular emphasis on electrodeposited coatings for electrical and electronic applications. Table 3 (References 6-55) summarizes the candidate substitute coatings referred to in the literature. The “best” replacement candidates resulting from this survey will be discussed here.

#### Metals

##### Aluminum

Aluminum is not easily applied as a coating by electrodeposition. The plating baths must be non-aqueous because of the reactivity of the metal and the displacement of hydrogen from aqueous

industrial atmospheres.<sup>54</sup>

Electroless nickel coatings can be heat-treated to provide a range of properties, depending on the phosphorus, boron or other minor alloying elements present.

Ni-P alloys, either plated or electroless plated, can be very smooth, bright and non-magnetic as well. Consequently, they have been used as an underlayer on magnetic storage disks for computers. Nickel used in other applications is more difficult to solder than cadmium. For electroless coatings, the difficulty increases as the phosphorus content increases, and especially if passivating films are formed by carrying out heat treatments in air. A mildly activated rosin flux can be used.<sup>32,34</sup>

Electroless nickel coatings can be applied to a uniform thickness on components having complicated shapes. Ni-B coatings have good electrical conductivity and are hard, and so find application on electrical contacts.<sup>38</sup> Nickel coatings, however, do have some utility as a replacement for cadmium in some applications.

Overall, the electrical properties of nickel coatings are similar to those of tin coatings. Like aluminum, the cost of applying nickel coatings—especially electroless nickel—is greater than for cadmium.

#### Silver

Silver coatings are soft and dull, as plated, and like nickel, may tarnish easily, especially in sulfur-containing environments. With the appropriate soldering technique, however, they are relatively easy to solder. Silver is not anodic to ferrous substrates; therefore, it affords corrosion protection by acting as a physical barrier.

Silver exhibits excellent electrical conductivity and can be used on contacts, but because of problems with electromigration in use—leading to soft shorts—a barrier coating is required as a post-treatment. The cost of silver may prohibit its use in some applications.

#### Tin

Tin “whiskers” can also cause soft shorts if they grow during use, and these are particularly a problem with bright deposits. It is said, however, that whisker formation is less likely than with cadmium or zinc. Bright deposits also present a problem with soldering because the occluded organic materials interfere with the soldering process.

Tin also forms a barrier coating, and electrodeposited coatings present less of a hydrogen embrittlement problem than

Table 4  
Main Features of Plating Baths  
For Candidate Nickel Alloy Coatings

Alloying Element	Conc. Range, %	Bath Type	Comments
Cobalt	18-35	Sulfamate/chloride	pH 3.5 to 4.48-55 C; low c.d.
Iron	5-64	Chloride, sulfate, sulfamate, sulfamate/chloride	pH 2 to 3, 25-40 C; low to medium c.d.
Zinc	5-8	Sulfate/chloride	acid bath, 25-40 C; low c.d.

some other metals. It is used as a substitute for cadmium on some electrical chasses.<sup>5</sup>

Polished tin is more widely used in Brazil as a replacement<sup>7</sup> because of its good appearance, ductility, solderability, low contact resistance and acceptable corrosion resistance. While resistance to outside environments is good, there is a problem with exposure to high humidity in closed spaces and to some volatile fatty acids, such as may be found in packaging and some wood products.<sup>7</sup>

Chromate-type conversion coatings are not required, and tin coatings exhibit good tarnish resistance compared to the other metals discussed.

Tin coatings may be applied by techniques other than electrodeposition (mechanical plating, electroless plating and ion implantation or mixing). The choice of technique will depend on the application and cost constraints. Nevertheless, tin coatings are being used for protection from electromagnetic interference, in selected areas, and as a replacement for gold on connectors. Tin can be reflowed to give a smooth, pore-free coating, but it easily cold-welds to itself. Seizing will occur if two tin-coated surfaces come into contact. While the contact resistance is not as low as that for freshly deposited zinc, over time the contact properties remain more stable.

#### Zinc

Zinc, like aluminum, is anodic to iron and provides sacrificial corrosion protection. It is not as good, however, as cadmium in high humidity or marine (high chloride) environments for extended periods.<sup>10,52</sup>

Zinc is reported to withstand exposure to SO<sub>2</sub> environments better than cadmium.<sup>53</sup>

The corrosion products are very voluminous, and can cause a problem where tolerances are small or appearance is important. In less aggressive environments, zinc tarnishes readily. For

maximum protection or for preservation of their bright appearance, zinc coatings must be given a chromate-type conversion coating or anodized.

Zinc coatings exhibit good adhesion, and the ductility depends on the type of plating bath used and the operating conditions. Deposits can be quite hard and deform less than their cadmium counterparts, resulting in poorer electrical contacts.<sup>17</sup> Lubricity is poor, but abrasion resistance is better than that of cadmium.<sup>54</sup>

Soldering, although not difficult for fresh deposits, can be problematical because a galvanic cell can be set up between the solder joint and the adjacent zinc coating, and the latter corrodes. If soldering must be done, it should be on a non-chromated surface, using a mildly activated rosin flux.<sup>7</sup>

Zinc may be applied by a number of commercially available processes, such as mechanical plating, electroplating and hot dipping (galvanizing). All are relatively low-cost techniques, and the latter gives thick, ductile coatings. Mechanically plated coatings tend to be thicker than electrodeposited coatings to provide the same degree of corrosion resistance. Barrel plating can be used for small components, and non-cyanide baths are available for electroplating.

While zinc is often suggested in general terms as a replacement for cadmium, especially on fasteners and small stampings, the only reference found for a specific electrical/electronic application was the use of a chromated, electrodeposited zinc coating for record player mechanisms.<sup>7</sup>

#### Alloys

Alloy deposition offers the opportunity of improving the properties of the basis metal or combining the best features of two or more metals. The alloy coatings referenced in the literature primarily have been applied by electrodeposition, al-

**Table 5**  
**Main Features of Plating Baths**  
**For Candidate Tin Alloy Coatings**

Alloying Element	Cone. Range, %	Bath Type	Comments
Cobalt	20	Sulfate	Alk. bath, inert anodes
Lead	2-10	Fluoborate, sulfamate, sulfonic	Acid bath operated at room temp.; low c.d.; Sn-Pb anodes
Nickel	33-35	Chloride/fluoride pyrophosphate	pH 2.5, 70 C; low c.d. insol. or soluble anodes; good throwing power
Zinc	15-30	Stannate/Zincate (CN)	Alk. bath with brighteners pH 12.5-13.0; 60-75 C; low c.d.

though some zinc “alloys” can be put down by mechanical plating techniques or by hot dipping. Tables 4-6 summarize the main features of the plating baths used to deposit zinc, tin and nickel alloys. Comments about the alloy coatings follow.

#### *Zn-Al*

Adding five percent aluminum to zinc improves the resistance of the latter to chloride, SO<sub>2</sub> and general atmospheric attack. The non-uniform distribution of the aluminum oxide on the surface, however, results invariable solderability.<sup>51</sup> Applied by hot dipping, the coating is bright, smooth and ductile, and exhibits good adhesion. It can be spot-welded, and if soldering is desirable, then an appropriate cleaning step with a NaOH or rosin flux should provide a good joint. Zn-Al coatings have been applied to wire.

#### *Zn-Co*

Another sacrificial coating is a Zn-Co alloy, containing either below 0.9 percent or above 1.5 percent cobalt.<sup>50</sup> Most applications to date have used between 0.2 and 0.6 percent cobalt, followed by a chromate-type treatment for maximum corrosion protection. The corrosion products include black spots resulting from the presence of the alloying element.

#### *Zn-Fe*

Zn-Fe deposits can provide sacrificial protection up to about 65 percent iron! An alloy in the range of 15-25 percent iron gives the best corrosion resistance, however.

#### *Zn-Mg*

To obtain manganese-containing alloys with improved corrosion resistance (>40 percent manganese), high current densities are needed. Corrosion protection is the result of the formation of manganous oxide on the surface.

#### *Zn-Ni*

Much more interest has been shown in Zn-Ni (or Ni-Zn) alloy coatings, with nickel contents typically in the range of 5-20 percent. These alloys exhibit better corrosion resistance than pure zinc in salt spray tests.<sup>51, 1055</sup> The ferrous substrates are also less likely to be affected by hydrogen embrittlement.<sup>55</sup>

As an example, a similarly prepared Zn-10Ni coating had about twice the resistance to salt spray as did cadmium, and five times that of zinc. For maximum corrosion protection, the plated components are given a hydrogen-relief bake, followed by a chromate-type conversion coating. Above about 20 percent nickel, the coatings are brittle and do not provide sacrificial protection to ferrous substrates.

Good ductility is obtained in the range of 5-15 percent,<sup>25</sup> while the 15 percent alloy exhibits good resistance to whisker growth. Zn-Ni coatings usually have good adhesion, are abrasion-resistant and can be used in environments up to 400 °F. They have been used on fasteners for electrical transmission structures and on television coaxial cable connectors instead of cadmium.<sup>57</sup>

#### *Zn-Sn*

A pyrophosphate/sulfate bath has been used to obtain Zn-Sn alloys, as opposed to Sn-Zn alloys, which are more prevalent, and for which commercial processes are available. Zinc is present normally in the range of 15-20 percent, and the deposits have an appearance similar to that of Cadmium<sup>5</sup> when electrodeposited. The alloys may also be applied as coatings by mechanical plating.

Some tarnishing occurs in marine environments, but the salt spray behavior is comparable to that of cadmium, as is

the lubricity of such coatings. Freshly deposited coatings can be soldered easily,<sup>7</sup> while a chromated surface on a Sn-22Zn alloy provides a low, stable contact resistance.<sup>58</sup> Sn-Zn alloy coatings exhibit good friction and wear characteristics, especially when lubricated, as well as good ductility. Electrical resistivity is relatively low,<sup>55</sup> but increases as the zinc content increases.

Alloys containing more than about 25 percent zinc become anodic with respect to iron, and therefore can provide some sacrificial protection. Sn-Zn alloys can be spot-welded. They are resistant to SO<sub>2</sub> and high humidity environments. One application is the coating of electrical chasses.<sup>55</sup>

#### *Sri-Co*

Sri-Co alloys, with about 20 percent cobalt, can be deposited from a mildly alkaline, sulfate-based plating bath using inert anodes. Specific applications were not identified.

#### *Sn-in*

Although not listed in Tables 4-6, these alloys find limited use because of their resistance to corrosion in salt water and ease of soldering. Brush plating, for example, is used to coat small areas for subsequent low temperature soldering of small components.<sup>14</sup>

#### *Sn-Pb*

The application of Sn-Pb coatings is relatively well-known, particularly in the printed circuit board (PCB) industry. The alloy coatings are less expensive than pure tin, are ductile, have similar appearance and corrosion resistance, and can be soldered easily. The coatings do tarnish, easily, however, and like tin, are susceptible to attack by some volatile organic compounds.<sup>19</sup> If the coatings are used on PCBs, all plastic components must first be properly cured. Alloys with 2-10 percent lead are preferred for electronic applications, because whisker growth is avoided.

Applications include small electronic components; over electrolytic nickel on lead frames, and occasionally on contacts. Contact resistance is not very low on aged deposits, and worse than for pure tin. For “make and break” sliding tabs on PCBs, however, the coatings are satisfactory.

#### *Sn-Ni*

Tin with 33-35 percent nickel corresponds to the intermetallic compound in that system. Consequently, the deposits are hard and brittle, and subject to impact

damage. Wear and abrasive resistance, on the other hand, are good.

As would be expected, corrosion protection is by a barrier mechanism. The coatings do not tarnish easily, nor are they susceptible to whisker growth. Sn-Ni coatings find application as an etch resist on PCBs because of their resistance to strong acids, and as a low-cost contact layer under gold on connectors.<sup>47</sup> Contact resistance is stable over time.

Freshly deposited coatings can be soldered without difficulty, but there tends to be some variability in the results obtained.<sup>48</sup> Other tin alloys are easier to solder and have lower contact resistance.

Other applications of Sn-Ni alloy coatings are on fuse caps, lugs, coaxial cable connectors, magnetic memory tapes (with a rhodium overlay), connectors and electrical switch gear. Application temperature is limited to about 650 °F, above which decomposition of the intermetallic compound occurs. The commercially available bath has good throwing power, and can be used for rack or barrel plating. Depending on the surface finish of the substrate (bright or matte), the deposit can have a similar appearance to chromium or stainless steel.

#### Nickel Alloys

##### Ni-Co

Limited data were found on nickel alloys. (Ni-P and Ni-B electroless deposits were discussed under nickel in the section on metals.) At one time, Ni-Co alloy coatings found some utility as "engineering" coatings, and for electroforming. The deposits are hard and wear resistant, but have a low internal stress. More recently, porous Ni-Co deposits, impregnated with a solid lubricant, have been promoted for applications requiring a combination of good wear and abrasion resistance, good corrosion resistance, and a low coefficient of friction.<sup>33</sup> These coatings have a high surface resistivity, and a dielectric constant and low dissipation factor that may be useful in some applications. Special treatments make the coatings conductive enough to provide anti-static properties.<sup>33</sup>

##### Ni-Fe

Some experimental studies of Ni-Fe deposition have been reported.<sup>31,42</sup> These studies were trying to produce materials with very low thermal coefficients of expansion for precision instruments and the like. For high iron contents, the sulfamate/chloride bath gave the best results. The deposits were bright and smooth. Electronic applications sug-

Alloying Element	Conc. Range, %	Bath Type	Comments
Cobalt	0.3 - 2	Chloride, sulfate	pH range 4.2 to 5.5, 10-50 C; low c.d. except sulfate bath
Iron	15-25	Chloride, sulfate	pH range 1.5 to 3.0, 15-50 C for sulfate, higher for chloride high c.d.
Manganese	> 4.0	Sulfate/citrate	acid bath, high cd. needed to co-deposit the Mn at these high concentrations
Nickel	5-20	Chloride, sulfate/sulfonate, sulfate/chloride, "alkaline" (zincate)	pH range 1.0 to 6.8, except for alk. bath, 20-90 C; low to medium cd. except sulfate/sulfonate bath
Tin	20-60	Pyrophosphate/sulfate	acid bath (compare with Sn-Zn alloy bath - Table 5)

gested<sup>42</sup> were cores for PCBs, microwave guides and laser housings.

#### Ni-Zn

Zn-Ni alloys have already been discussed. One reference, however, did describe an alloy of nickel with 5-8 percent zinc, deposited from a sulfate/chloride bath at low current density. It is not clear what benefits might arise from adding such a small amount of zinc.

#### Mixtures

Reference 8 states that a silver-plus-tin oxide coating may be used as a substitute for a silver-plus-cadmium oxide coating for low voltage, electromechanical switch gear. A translation of the reference was not available at the time

this survey was conducted; details are therefore not available.

A proprietary process exists whereby phosphates and silicon compounds are occluded in zinc electrodeposits.<sup>44</sup> An acid bath is used at a low current density to give coatings with good corrosion resistance. A chromate treatment further improves the corrosion resistance. Adhesion is good, galling resistance is relatively low, and the coatings render the ferrous substrates less susceptible to pitting attack and stress-corrosion cracking. The coating might be used on fasteners, small stampings and chasses.

Electroless nickel deposits have been discussed. It is possible to codeposit particles such as boron or titanium nitride, silica, alumina or solid lubricants.

Metal	Max - service Temp., F	Electrical Resistivity, $\mu$ ohm-cm	Salt Spray Resistance, hr(°)
cd	450	6.8-8.5	>150
Al	930	2.8 -3.8	>= 150
Ni (E' less)	900 <sup>(b)</sup>	20-60	> 50
Ni (E' dep)	900	72-7.7	-
Ag	965	1.6	--
Sn	< 450	11.4	>= 45
Zn	500	5.9-7.5	>= 72

(a) ASTM B-117; hours to red rust 0.0003-inch coating, not chromated.  
(b) Depends on heat treatment received.

**Table 8**  
**Summary of Some Properties**  
**Of Alloy Coating Candidates**

Alloy <sup>(a)</sup>	Max. Service Temp., F	Electrical Resistivity, $\mu$ ohm-cm	Salt Spray Resistance, hr <sup>(b)</sup>
Ni-Co	--	11.6	--
Ni-Co + PTFE	--	60	$\geq 475^{(c)}$
Sn-Pb	< 360	13.4	--
Sn-Ni	660	--	--
Sn-Zn	--	14.7	> 700
Zn-Al	--	--	$\geq 300$
Zn-Co	--	--	$\geq 450$
Zn-Fe	--	--	> 300
Zn-Mn	--	--	- 1000
Zn-Ni	- 400	--	> 750
Zn-Sn	--	--	> 250

(a) Values given for optimum composition.

(b) ASTM B-117; hours to red rust, 0.0003-inch coating, not chromated.

(c) 0.001-inch coating.

For applications requiring good corrosion resistance along with good wear or abrasion resistance or lubricity, such additions might be useful.

Some mechanically plated coatings may be considered to be mixtures rather than alloys. Examples are zinc-plus-aluminum and tin-plus-zinc, where the particles may be intimately mixed. These types of coatings are usually applied to fasteners and small stampings, rather than being used for electrical/electronic applications. Their advantage is that the application technique is less likely to cause hydrogen embrittlement of the substrate.

### Compounds

Compounds, such as titanium nitride, deposited as thin coatings, have a pleasing appearance. Adhesion is fair, and the coatings tend to be hard and brittle. Such deposits—applied by vapor deposition techniques—exhibit good wear and abrasion resistance, but tend to be more porous than electrodeposited cadmium coatings.<sup>5</sup> As a result, corrosion resistance may be less than desirable. Such coatings find limited application.

Silicates, deposited by an electrophoretic technique and subsequently fused, provide hard, glassy

coatings with good corrosion resistance, particularly in acid environments.<sup>23</sup> Substrates such as aluminum, magnesium, titanium, niobium and tantalum—or their alloys—may be coated by this commercial process. Applications are said to be found in the automotive and electronic industries, as well as in solar panels. Details, however, were not provided.

### Most Promising Candidates

While a number of possible alternative coatings to cadmium have been suggested in the literature for application in the electrical/electronic industries, none can match all the desirable properties of cadmium—although for some specific applications, certain alternatives appear to be acceptable. Tables 7 and 8 summarize some of the property data available.

Corrosion data are difficult to interpret because the references do not always specify if a conversion coating has been used. If it has, the type of coating is not always specified. In addition, coating thickness may not be given. The data in the tables, therefore, should only be used as a guideline to relative performance. The values may vary widely with composition, heat treatment, presence of impu-

rities in the deposit, and so on.

The most "promising candidates identified in this survey as alternatives to cadmium are:

- Electroless nickel (Ni-P, Ni-B)
- Electrolytic tin
- Electrolytic Sri-Co, Sn-Pb, Sn-Zn & Sn-Ni
- Electrolytic Zn-Ni.

The composition and thickness of the coatings will depend on the specified requirements. In some cases, post-treatments will be required to maximize corrosion resistance or to remove hydrogen. The use of chromate-type conversion coatings, however, is another problem to be addressed if the coating system truly must be non-toxic or non-polluting.

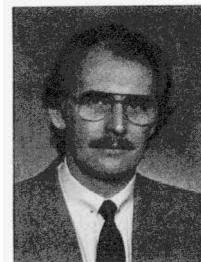
Many of the candidate coatings appear on the list of candidate, but untested, replacements for cadmium in a survey of manufacturers, suppliers and military users (in certain stock classes) that was conducted by the Defense Electronics Supply Center as part of its "Hazardous Materials Minimization Program."<sup>29</sup>

### References\*

1. R. Marce, "ITT Connects with Cadmium; *Plat. & Sur. Fin.*, 69,28 (Nov. 1982).
2. B.A. Graves, "Industrial Toxics Project: The 33150 Program," *Prod. Fin.*, 56,132 (Sept. 1992).
3. E.W. Brooman et al, "Cadmium Plating Source Substitution; Final Report to Defense Construction Supply Center, Columbus, OH (1 989).
4. F. Altmayer, "Pollution Prevention: Both Sides," *Plat. & Sur. Fin.*, 79, 23 (Aug. 1992).
5. E.H. Lesser, "Alternatives to Cadmium Plating: Reflections Five Years Later," *Plat. & Sur. Fin.*, 69,34 (Nov. 1982).
6. P. Baeyens, "No More Cadmium Plating? Is There a Substitute Process?," *Surfaces*, 17, 50(1 978).
7. P. Baeyens, "No More Cadmium Plating? Are There Processes to Replace It?," *Galvanotechnik*, 68,590 (July 1977).
8. N. Behrens, "Substitution for Cadmium in Low Voltage Switch Apparatus Engineering," *Villamossag*, 35,76 (Feb/Mar 1987).
9. C.J. Burkitt, "Is Zinc Plating Good Enough for a Safe Earth?," *Electr. Rev.*, 213, 28 (Sept. 1983).
10. J.W. Dini and H.R. Johnson, "Electrodeposition of Zinc-Nickel Alloy Coating," *Proc., Workshop Alt. Cadmium Electroplate. Met. Fin.*, 171 (Gaithersburg, MD, 1979).
11. F.C. Eversteijn, "Zinc and Tin as Alternatives for the Use of Cadmium in the Electronics Industry," *Constructeur* 18,34 (Mar. 1979).
12. F.C. Eversteijn, G. Krijl and A.W. Deursen, "Zinc and Tin as Alternatives for the Use of Cadmium in the Electronic Industry,"

- Belg-Ned. Tijdschr. Oppervlaktetech. Mater.*, 23,28 (Feb. 1979).
13. E. Furka, K. Neemes and R. Kahan, "Replacement of Cadmium by Zinc Coatings with Special Reference to Low Temperature Resistance," Proc. 6th Symp. on Electroplating, 96 (Budapest, Hungary, 1985).
  14. R. Marce, "ITT Cannon Connects with Cadmium; Plat. & Sur. Fin., 69,28 (Nov. 1962).
  15. D.E. Muehlberger, "Plating with Aluminum by Ion Vapor Deposition," SAE Conf. Proc. (1978).
  16. M. Rubenstein and A. Rosen, "Electrochemical Metallizing Tin and Tin Alloy Applications," Plat. & Sur. Fin., 75, 34 (Aug. 1988).
  17. E.M. Walsh, "Zinc as a Substitute for Cadmium," *Finishing*, 6,13 (June 1982).
  18. P.S. Wilcox, "Uses of Electroplated Cadmium," Proc. *Cadmium 86,65* (San Francisco, CA, 1986).
  19. A.H. Chapman, W.B. Hampshire and D.J. Maykuth, "Tin Coatings: Present & Future," *Plat. & Sur. Fin.*, 70, 40 (Dec. 1983).
  20. V.L. Holmes, D.E. Muehlberger and J.J. Reilly, "The Substitution of IVD Aluminum for Cadmium," Final Report, Data Base Handbook C87-10162, Dept. of Air Force (1 989).
  21. C.V. Lundberg, "Longterm Weathering of Organic and Inorganic Coatings on Steel and Aluminum," *Polym. Mat. Sci. Eng.*, 58,405 (1 988).
  22. R.P. Tracy and T.W. Bleeks, "Using Electroless Nickel Coatings; *Mat. Engrg.*, 38 (Nov. 1989)
  23. "Silicate Coating Process—Fast and Tough," *Ind. Fin.*, 57,41 (June 1981).
  24. G.G. Kraft, "The Future of Cadmium Electroplating," *Met. Fin.*, 88, 29 (July 1990).
  25. R.G. Baker and C.A. Holden, "Investigation of Zinc-Nickel Alloy Electrodeposits-Part I, Rack Plating," *Proc. 71st AES An. Tech. Conf.* (1 984).
  26. I.V. Kadija, J.C. Fister, J. Winter and A. Parthasarathi, "Whisker Resistant Tin Coating and Baths for Making Such Coatings," U.S. patent 4,749,626 (1 988).
  27. M.W. Bayes, "Electroless Nickel in the '90s," *Met. Fin.*, 88,27 (April 1990).
  28. E. Yang, S.K. Doss and P. Peterson, "Corrosion of Electroless Ni-P-Cu Alloy in an Atmospheric Gas Chamber," *Plat. & Sur. Fin.*, 75,60 (Dec. 1988).
  29. M. Matsuoka, S. Imanishi and T. Hayashi, "Physical Properties of Electroless Ni-P Alloy Deposits for a Pyrophosphate Bath," *Plat. & Sur. Fin.*, 78,54 (Nov. 1989).
  30. T. Kate, T. Ito and M. Maeda, "Chemical Vapor Deposition of Aluminum Enhanced by Magnetron-Plasma," *J. Electrochem. Soc.*, 135,455 (Feb. 1988).
  31. P.C. Andricacos, C. Arana, J. Tabib, J. Dukovic and L.T. Romankiw, "Electrodeposition of Nickel-Iron Alloys," *J. Electrochem. Soc.*, 135, 1336(1938).
  32. D.M. Rapp, "The Solderability of Electroless Nickel Coatings," *Electroless Nickel News*, 2,4 (Feb. 1986).
  33. "Nedox Synergistic Coatings," General Magnaplate Corp., Linden, NJ (1989).
  34. "Plating Enhances Corrosion Resistance and Solderability," *Prod. Fin.*, 42, 34 (Dec. 1989).
  35. S.J. Blunden, "Tin-Zinc Coatings," I.T.R.I. Leaflet L80, I.T.R.I. (1990).
  36. J. Henry, "A New Fluorinated Electroless Nickel Codeposit," *Met. Fin.*, 88,15 (Oct. 1990).
  37. "Tin and Tin Alloy Coatings; *MFSA Quality Metal Finishing Guide*, 1 (1987).
  38. M. Bayes, "Electroless Nickel in the '90s," Shipley Catalyst (1990).
  39. "Another Coating Dimension: *Prod. Fin.*, 56,60 (May 1992).
  40. N. Zaki and E. Budman, "Zinc Alloy Plating Today," *Prod. Fin.*, 56,48 (Jan. 1991).
  41. "Sn-Zn Alloy Electroplates Outperform Cadmium Deposits," *Adv. Mat. & Proc.*, 140,37 (June 1991).
  42. D.L. Grimmer, M. Schwartz and K. Nobe, "Electrodeposition of Iron-Nickel (Invar) Alloys," *Plat. & Sur. Fin.*, 75, 46 (June 1988).
  43. N. Phan, M. Schwartz and K. Nobe, "Iron-Nickel, Iron-Nickel-Cobalt Electrodeposition," *Plat. & Sur. Fin.*, 75, 46 (Aug. 1988).
  44. N.A.G. Ahmed and K. Watkins, "Ion Assisted Deposition for Surface Engineering," *Finishing*, 15, 23 (June 1991).
  45. W. Kautek, W. Fromberg and J.A. deHek, "Galvano-Aluminum: Process Engineering and Applications," *Metaloberflache*, 46,67 (Feb. 1992).
  46. J.M. Bowden, "New Prospects for Tin-Nickel Coatings; I.T.R.I. Publication No. 720, *Metal Bul. Monthly* (April 1991).
  47. "Tin-Zinc Coatings from the I.T.R.I. Stanzec Process," I.T.R.I. Data Sheet No. DS9.
  48. "Tin-Nickel Coatings: Versatility and Performance," I.T.R.I. Data Sheet No. DS10.
  49. K.W. Rizzi, N.J. Spiliotis and K.F. Blurton, "New Zinc Electroplate Fights Both Wear and Corrosion," *Met. Prog.*, 129,51 (Feb. 1986).
  50. R. Winand, "Continuous Strip Coating: New Zinc Alloy Tailored Coatings," *Surface Coatings Tee.*, 37, 65(1 989).
  51. F.E. Goodwin, "Galfan Galvanizing Alloy and Technology," ILZRO Publication, 2nd Ed., 1984.
  52. B. Knotkova, E. Boubelova and J. Mechura, "Alternative to Cadmium Coatings," *Koroze Ochr. Mater.*, 27, 25 (Feb. 1983).
  53. L. Nanova, V. Kozhukharov and V. Velinov, "Zinc, Cadmium and Cadmium-Zinc Coatings, Part 2—Testing Under Natural Atmospheric Conditions," *Galvanotechnik*, 76,453 (April 1985).
  54. M. Ingle and T. Marchesani, "Evaluation of Environmentally Acceptable Substitutes for Cadmium Plating," *SAE Proc.* (1991).
  55. G. Hsu, "Zinc-Nickel Alloy Plating: an Alternative to Cadmium," *Plat. & Sur. Fin.*, 71,52 (April 1984).
  56. H. Simon, "Alternatives to Cadmium Plating," *Ind. Prod. Eng.*, 9, 40 (July 1985).
  57. N. Zaki and E. Budman, "Zinc Alloy Plating Today," *Prod. Fin.*, 56, 46, (Nov. 1991).
  58. "Tin and Tin Alloy Coatings," *MFSA Quality Metal Finishing Guide*, 1 (1987).
  59. D.E. Moore, Defense Logistics Agency, personal communication (Nov. 1992).

\*Editor's Note: Because Dr. Brooman's literature survey is a valuable one and lengthy, we deviated from P&SFs usual reference style in order to provide titles of articles. Readers who are interested in studying some of the referenced articles can thereby quickly focus on specific areas.



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Dr. Eric W. Brooman is a research leader in the Metals and Ceramics Department (a not-for-profit contract R&D laboratory) and manager of the Electrochemical Technology Group at Battelle, Commercial & Industrial Technology Division, 505 King Avenue, Columbus, OH 43201. Originally from England, Dr. Brooman has an honors degree in metallurgy and a PhD from Cambridge University in metallurgy for electrochemical research. In the early '70s, he was a research fellow in electrochemistry at the University of Salford in England. Dr. Brooman's career has included serving as a consultant, university lecturer and researcher. His current interests are materials related, whether for energy conversion and storage, metal finishing, or waste minimization and metals recovery recycling and reuse.