Alternatives to Cadmium Plating for Detail Parts

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Version **1**

Purpose: This report is generated by IAEG WG2 Replacement Technologies, for the purpose of comparing publicly available information on alternatives to cadmium plating for detail parts.

Audience: This Report is intended for Public Release.

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Version History

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1 Purpose and Scope

This report has been compiled to provide guidance to IAEG WG2 member companies and the public coating community regarding cadmium electroplating, its regulations, and alternative electroplating systems. The scope of the report is limited to the discussion of cadmium plating, specifications, properties, applications, and comparison with other plated systems. Cadmium alloy plating, non-conductive coatings including proprietary coatings, diffused, vacuum, ion vapor or mechanically deposited coatings are not covered in this report. Specifically, this report covers cadmium plating and alternative plating for detail parts, with a detail part defined as a single, non-divisible component, which may form part of a larger assembly. Detail parts may be standard parts or unique designs. Cadmium plating alternatives for non-detail parts are considered by the IAEG WG2 Project "Cadmium Plating for Industry Standard Parts".

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- Thiru Munisamy – Raytheon
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2 Cadmium Electroplating

2.1 Cadmium Metal and Compounds

Cadmium (Cd) is a silvery-white, soft, and ductile metal with an atomic number of 48. Cadmium has a melting point of 610 °F (321 °C) and forms many covalent and ionic compounds in the +2-oxidation state such as cadmium carbonate, cadmium chloride, cadmium fluoride, cadmium hydroxide, cadmium nitrate, cadmium oxide and cadmium sulfide. Cadmium is a byproduct of the zinc manufacturing process with limited availability in the earth's crust and is widely used in protective coating systems, pigments, electrical bonding applications, and as a component in solar cells and batteries.

2.2 Cadmium Electroplating Process and Specifications

Electrodeposition/electroplating of cadmium metal on detail parts provides functional value. For example, it has been used as a sacrificial corrosion protective coating for ferrous metals (e.g., low alloy carbon steel). Cadmium is predominately plated from a cyanide bath, consisting of sodium cyanide, cadmium oxide, sodium hydroxide and organic/inorganic addition agents and brighteners (Typical plating parameters are 0.5 – 5 A/dm^2 current density, 20-30 °C, steel anodes) [1]. The resulting coating is dense and fine-grained. Cleaning steps for ferrous alloys before plating can include an alkaline soap cleaner to remove oil/grease/contaminants/FOD, followed by an alkaline electrocleaner step to remove oxides and finally an acid dip activation step. The cleaned parts shall exhibit a water break free surface before plating. After cadmium plating, typically a chemical conversion coating is applied for added corrosion protection.

A few common cadmium plating industry specifications are AMS-QQ-P-416, AMS2400, MIL-STD-870. AMS-QQ-P-416 is widely used in the aerospace industry and specifies different Types, Grades and Classes [2]:

- Type I - As plated
- Type II - With supplementary chromate treatment
    - Grade A - Hexavalent chromate treatment with a maximum service temperature of 150 °F
    - Grade B - Hexavalent chrome free treatment with a maximum service temperature of 375 °F
- Type III - With supplementary phosphate treatment
- Class 1: 0.0005 inch minimum
- Class 2 - 0.0003 inch minimum
- Class 3 - 0.0002 inch minimum

AMS-QQ-P-416 requires cadmium plating with a conversion coating to withstand 96 hours of salt spray testing in accordance with ASTM B117 without white corrosion formation.

2.3 Applications, Properties and Limitations of Cadmium Plating

Cadmium plating has been used on aircraft structures, engine components, propellers, landing gears and actuators for many decades owing to several important functional properties such as high conductivity, excellent sacrificial corrosion protection, galvanic compatibility, lubricity, anti-galling, good torque-tension properties and solderability. Limitations of cadmium plating include sublimation in vacuum environments (space application is prohibited), cadmium whiskers, cadmium bloom, incompatibility with carbon composites and titanium alloys, and hydrogen embrittlement susceptibility for high strength steel during the plating process.

2.4 Cadmium Toxicity and Regulations

Cadmium is a toxic heavy metal and exposure to it results in acute and chronic health effects [3] [4]. Ingestion and inhalation are the primary means of exposure. Exposure can also be via the environment (air, water or soil).

- Acute oral exposure may lead to gastrointestinal irritation, vomiting, abdominal pain and diarrhoea. Higher doses may lead to renal failure and death.

- Acute inhalation will initially cause irritation of the upper respiratory tract, and can then lead to pulmonary oedema, bronchitis, chemical pneumonitis, up to respiratory failure and death.

- Chronic oral exposure can lead to renal failure, characterized by proteinuria.

- Chronic inhalation leads to loss of renal function, and impairs lung function, can lead to bronchitis, obstructive lung disease and interstitial fibrosis.

- Cadmium is a category 1 carcinogen; inhalation of cadmium increases the risk of lung cancer.

The cadmium plating process has three main risk areas for exposure. Firstly, at the facility applying the coating, employees are at risk of inhalation or ingestion from the cadmium plating process bath, and/or powdered components such as cadmium oxide. Secondly, there is a risk of accidental discharge into the environment from these facilities (e.g., spillage of bath solution onto ground water). Finally, if the cadmium plating comes into contact with acid vapours (from wood during storage or transit), it can develop what is known as "cadmium bloom" on the surface. The bloom is highly toxic in both soluble and respirable forms, affecting the health and safety of those handling cadmium plated components.

As such, cadmium has become highly regulated in many jurisdictions. In the US, cadmium appears on the EPA's Integrated Risk Information System [5] , and OSHA's Workplace Exposure Limits [6]. There are over 50 countries with safety or environmental legislation relating to cadmium. The majority of these laws do not deal specifically with cadmium plating, but with waste treatment, occupational exposure, and exposure to the public via consumer products. In the EU, REACH legislation has a Restriction on the use of cadmium [7]. For example, there is 0.01 % by weight (wt.%) limit of cadmium in various products such as paints, plastics, brazing fillers and jewellery. The legislation specifically mentions cadmium plating, however, there is an exemption to this restriction for "articles used for safety purposes in aeronautical, aerospace, mining, offshore and nuclear sectors, in road and agricultural vehicles, rolling stock and vessels, and in electrical contacts". This exemption has allowed the aerospace and defence industry to continue the use of cadmium plating, though efforts are being made to reduce reliance on this toxic substance given the risks posed, and ever-increasing regulatory burden on processors and users.

3 Alternatives to Cadmium Plating

A list of properties for cadmium plating and possible alternatives is shown in Table 1. One must choose an alternative to cadmium plating based on equivalent or better functionality specific to an application [8]. Some alternatives such as zinc-nickel plating may use a conversion coating containing hexavalent chromium compound, which is a carcinogenic and heavily regulated substance; therefore, the alternative needs to be selected prudently.

3.1 Zinc-Nickel Plating

Zinc-nickel (Zn-Ni) plating has been widely proposed as an alternative to cadmium plating for detail parts. The alloy system with 6-20 wt.% nobler nickel metal is better than pure zinc plating and exhibits a reduced corrosion rate but still acts as a sacrificial layer similar to cadmium and zinc plating. A nickel concentration of 12-16 wt.% in the coating corresponds to peak corrosion resistance performance, while the sacrificial characteristics are reduced when nickel is greater than 16 wt.%. The plating can be performed from an acid or alkaline non-cyanide bath, with the alkaline process preferred for high strength steel to mitigate the hydrogen embrittlement risk from the plating process. AMS2417 and AMS2461 are commonly used Zn-Ni plating specifications. AMS2417 specifies 6-20 wt.% nickel composition while AMS2461 specifies 12-16 wt.%. AMS2461 requires plating from an alkaline solution and only permits trivalent chromate and phosphate conversion coatings. Both AMS2417 and AMS2461 require the coating to withstand 96 hours of salt spray testing in accordance with ASTM B117 without white corrosion formation and 500 hours of salt spray testing per ASTM B117 without red corrosion formation for ferrous parts. The Zn-Ni operating temperature (i.e., 500 °F maximum) is slightly higher than cadmium plating operating temperature (i.e., 450 °F maximum). The Zn-Ni plating functional lifetime is increased by a conversion coating, however, caution should be used when specifying the conversion coating type as some chemistries contain hexavalent chromium and cobalt, which are Substances of Very High Concern (SVHC) under EU REACh regulation. For hexavalent chromium and cobalt free coatings, refer to AMS2417, Type 2 Grade B (trivalent chromium based) and AMS2461 Type 2 Grade A (trivalent chromium based) and AMS2461 Type 2 Grade B (trivalent chromium based and cobalt free).

3.2 Tin-Zinc Plating

Tin-Zinc plating (Sn-Zn, 70-90 wt.% tin, 10-30 wt. % zinc) is a superior coating for solderability and lubricity with corrosion resistance requirements equivalent to cadmium plating (i.e., Salt spray testing in accordance with ASTM B117: 96 hours (no white corrosion), 500 hours (no base metal corrosion or red rust for ferrous alloy)). Traditionally, Sn-Zn plating is used for electrical contacts with suitable properties such as reduced whisker growth (in comparison to pure tin plating) and high electrical conductivity. The Sn-Zn alloy melting point is 512 °F, a service temperature of 375 °F maximum is defined in the AMS2434 specification. Predominantly, a sodium stannate/zinc cyanide bath is used for plating, and cyanide toxicity is well known. Regarding material availability, zinc and tin are widely available compared to cadmium.

3.3 Electroless Nickel Plating

The electroless nickel (EN) plating process involves chemical deposition where nickel ions are reduced to nickel metal using a hypophosphite reducing agent. Phosphorus is deposited with nickel metal during the process and ranges from 2 to 13 wt.%. When sodium borohydride or dimethylamine borane is used as a reducing agent, boron is co-deposited. The property of the coating is heavily dependent on the alloy content (e.g., phosphorus or boron) and tunable. The coating is a barrier type because it is nobler than the substrate, unlike cadmium plating. The plating bath can be acidic or alkaline, however the acidic type is in common use/practice. The temperature of the bath ranges between 180 and 195 °F, and the substrates need suitable activation or pretreament before coating. Deposition occurs uniformly with excellent throwing power for complex geometries unlike electroplating. The coating exhibits excellent hardness, a low coefficient of friction (when coated with PTFE (Polytetrafluoroethylene)), corrosion resistance, solderability, high service temperature, and wear resistance properties (see Table 1). Common specifications related to EN plating include AMS2404, ASTM B733, AMS-C-26074, and AMS2454 (EN-PTFE).

3.4 Electrolytic Nickel Plating

Electrolytic nickel plating is typically used as barrier underplate and as a coating on corrosion resisting steels for connectors applications (refer to MIL-DTL-38999). The plating is highly ductile with a high service temperature. The plating is carried out from a Watts bath (nickel sulfate and nickel chloride chemistries) or a nickel sulfamate bath, of which the sulfamate bath with no addition agents provides a low stress functional coating and is widely used on aerospace components. Electrolytic nickel plating is not a preferred replacement for cadmium but for some applications and designs, it may be considered as an option (it is a harder coating than Zn-Ni and Sn-Zn and cheaper than EN). Refer to the AMS-QQ-P-290 specification for designs requiring this plating.

3.5 Aluminum Plating

Aluminum plating is an alternative to ion vapor deposited aluminum coatings and cadmium plating. It is applicable to high strength steel alloys which are prone to hydrogen embrittlement. This high purity aluminum plating is produced from a non-aqueous aprotic electrolyte, and provides both sacrificial and barrier protection (plating with chromate conversion coating) to the substrate metal.

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The plating provides high corrosion resistance (salt spray (ASTM B117) protection for 672 hours in accordance with MIL-DTL-83488), high temperature applicability (up to 1000 °F) and is considered as a drop-in replacement for cadmium for many applications (e.g., space applications with an operating temperature of 1000 °F, plating on high strength steel with no hydrogen embrittlement) [9]. In the MIL-DTL-83488 specification, a hexavalent chromium conversion coating is listed as the supplementary treatment. To eliminate toxic and REACH restrictive components, a non-hexavalent conversion coating should be considered to reduce environmental or regulatory concerns.

3.6 Tin-Nickel Plating

Tin-nickel (65-35 wt.% composition, 600-700 VH) electroplating is also available. Refer to ASTM B605 - Standard Specification for Electrodeposited Coatings of Tin-Nickel Alloy to assess its properties for use as a replacement for cadmium plating. Note data for this plating type is not readily available, therefore it has been excluded from Table 1.

4 Final Notes and Design Considerations

Zinc-nickel plating is considered a good alternative to cadmium plating for detail and structural parts. Other alternatives are available, and the suitability of a plating for a given part/assembly should be based on testing, performance, properties (see Table 1) and environmental conditions. Galvanic compatibility of coatings and metals is a critical factor in design, and galvanically incompatible design (e.g., cadmium plating in contact with magnesium metal (wet assembly required to mitigate)) can result in accelerated corrosion. For galvanic compatibility of cadmium, alternatives, and other metals/coatings, refer to MIL-STD-889. Another design consideration is the use of alternative base metals, for example in some instances, stainless steels which are ferrous based corrosion resistant alloys containing >16 wt.% chromium can be substituted for carbon and low alloy steels with no corrosion protection coating on them. Cadmium and alternative plating listed in this report can be primed and painted except EN-PTFE. The presence of a conversion coating on the metal coating helps with primer adhesion, however if no conversion coating is present, mechanical surface preparation and/or wash/etch primer application may be needed for adequate adhesion (for example, painting on electroless nickel).

Table 1 Comparison of Properties of Cadmium Plating and Alternative Coatings [1] [10] [11] [12]

Properties and Attributes	**Cadmium Plating**	**Zinc-Nickel Plating**	**Tin-Zinc Plating**	**Electroless Nickel Plating**	**Electrolytic Nickel Plating**	**Aluminum Plating**
Hardness		393 – 472 HV		773 HV 100	400 HV or equivalent	22 – 25 HV 0.015
Corrosion Resistance (ASTM B117)	96 hours (no white corrosion)	96 hours (no white corrosion) 500 hours (no base metal corrosion)	96 hours (no white corrosion) 500 hours (no base metal corrosion)	48 hours (no corrosion), 2000 hours (no corrosion for Ni-PTFE)	48 hours (no corrosion)	672 hours (no base metal corrosion)
Specification (examples listed)	AMS-QQ-P-416, AMS4200, MIL-STD-870	AMS2417, AMS2461, MIL-PRF-32660	AMS2434	AMS2404, AMS2405, ASTM B733, AMS-C-36074, AMS2454 (EN-PTFE)	AMS-QQ-P-290, AMS2403, AMS2423	MIL-DTL-83488
ROHS compliance	No	Yes	Yes	Yes	Yes	Yes
Composition	100% cadmium	6 – 20 % nickel, remainder zinc	70 – 90 % tin, 10 – 30 % zinc	1 – 3 % phosphorous, remainder nickel	100% nickel	99%+ aluminum
Solderability			Yes	Yes	Yes	
Ductility				1 – 2.5 % elongation to fracture	2 – 30 %	
Coefficient of Friction	0.25-0.35			0.2 (Ni-PTFE)		0.16
Electrical Properties				30 – 100 x 10^{-6} ohm-cm	7.8 x 10^{-6} ohm-cm	
Service Temperature °F	<450	500	375	750	>400	<925 – 1000
Wear / Abrasion Resistance	1.8 – 3.6 x10^{-8} mg/cm			4 mg/1000 cycles Taber wear		28 mg/1000 cycles Taber wear
Supplementary treatment with hexavalent chromium compounds	Yes	Yes	Yes	No	No	Yes
Supplementary treatment with non-hexavalent chromium compounds	Yes	Yes	Yes	No	No	No
Thickness (inches), range	0.0002 – 0.0005	0.0002 – 0.0007	0.0003 – 0.0005	0.0005 – 0.0015	0.0001 – 0.0016	0.0003 – 0.0010

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