Chapter 23 – REPLACING CADMIUM AND CHROMIUM

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23.1 INTRODUCTION

Electroplated cadmium and hard chromium have been used extensively [1]-[7] and [8] as protective coatings for the most demanding aerospace applications in aggressive environments. Despite excellent technical performance and low deposition costs, these coatings are heavily regulated because both materials and/or their deposition technologies present serious health and environmental hazards. Cadmium, for example, is highly toxic in its metallic form and the plating bath contains cyanides. Thus, both the coating and the deposition process are potentially harmful. Chromium, on the other hand, is completely benign in its metallic form. However, the most common deposition process for so-called hard chromium utilizes highly toxic hexavalent chromium solutions based on chromic acid, and is the subject of strict environmental regulations. The regulatory limitations increase the life cycle cost of these materials/coatings and many countries or municipalities effectively prohibit the use of hard chromium or cadmium plating.

There is a tendency, especially evident in Europe and Japan, but also in the U.S.A. and Canada to further tighten respective environmental legislations, thus leading to a complete ban on the industrial use of cadmium and hexavalent chromium [9]-[11]. The general industry has been working under cadmium and hexavalent chromium bans for years, while the aerospace and military have been exempt from the respective regulations. However, growing legislative pressure and logistic issues are forcing aerospace and military agencies to adapt to changing standards and to look for viable alternatives. However, both cadmium and hard chromium are low-cost coatings that have unique properties making them difficult to replace on a one-to-one basis. The so-called drop-in replacements are especially sought by the aerospace industry since the required engineering changes for large numbers of component drawings would be cost-prohibitive. On the other hand, in new designs such as the Joint Strike Fighter, there is a general policy to avoid using cadmium and hard chromium coatings entirely [12].

Despite different properties and areas of applications for cadmium and hard chromium coatings, there have been some similarities in the approach to finding the cost effective and technically viable alternatives. Firstly, it became clear from the beginning that no single coating could replace either cadmium or hard chromium in all respective applications. Instead, it was realized that the protective function of the coating needed to be specifically determined for a given application, so that an alternative coating could be effectively selected. Besides technical performance, other important factors such as overall cost (from cost of deposition, through maintenance to disposal to coated parts) and wide availability of the alternative coating technology need to be considered. For the latter issue, the main concern is the dependence on proprietary technologies since this usually means limited availability and complicated logistics. Secondly, there is a general trend to replace “wet” processes, such as electroplating, with non-embrittling “dry” technologies such as thermal spraying or vacuum-based deposition techniques. This trend is a result of the hydrogen embrittlement that occurs in the wet processes. Hydrogen embrittlement is a concern for many aerospace applications where high strength steels are used (e.g., landing gear components and fasteners). Although baking can eliminate hydrogen, the process is highly energy-demanding and thus costly. Consequently, elimination of hydrogen at source from the deposition process would be advantageous for any alternative technology.

There are many potential alternatives for both hard chromium and cadmium. In recent years, several detailed reviews of cadmium and hard chromium alternative coatings for use in aircraft applications were prepared, among others [6],[7],[12] and [13]. This review provides highlights of major findings and new developments.

23.2 ENVIRONMENTAL LEGISLATION

Since the hexavalent chromium (Cr (VI)) is known human carcinogen, air emission and wastes from hard chromium plating operation must comply with environmental legislations specifying emissions standards and permissible exposure limits. In the case of cadmium the problem is even more serious and widespread since the toxic metal is carried with the plated part throughout its entire life cycle, creating hazardous conditions whenever these parts are treated or handled. The legislations in given countries (or even provinces or municipalities) are different, although the common goal is to heavily restrict the use of cadmium and hexavalent chromium, leading to complete ban.

23.2.1 Canada

In Canada, both inorganic cadmium compounds and hexavalent chromium compounds are on the Toxic Substances List that is part of the Canadian Environmental Protection Act (CEPA) [A1]. The CEPA was passed by Canadian Parliament in 1999 and came into force on March 31, 2000. Since then it has been continuously updated, with the latest revision of the Schedule 1 (Toxic Substances List) dated on December 27, 2006. Included on this list are oxidic, sulphidic and soluble inorganic nickel compounds, which may complicate the development of electrolytic hard chromium and cadmium alternatives.

23.2.2 U.S.A.

The regulatory bodies in the U.S. are the Environmental Protection Agency (EPA) and the Occupational, Safety and Health Administration (OSHA). The relevant regulations concerning cadmium, hexavalent chromium and other hazardous materials are including in the Clean Air Act (CAA) [A2] and Toxic Substance Control Act [A3].

As an example of current and incoming regulations, in February 2006, OSHA lowered Permissible Exposure Limit (PEL) for Cr(VI) in electroplating to 5 $\mu g/m^3$. The EPA, on the other hand, is now considering new rules to be issued in 2008 that may affect not only the use of cadmium and hexavalent chromium but also nickel and cobalt compounds. Interestingly, California recently issued new air rules for thermal spray operations such as HVOF that may affect one of the main technologies for hard chromium replacement.

23.2.3 Europe

For years, European Union (EU) has been driving force in setting health-protective standards in use of hazardous materials. Some of the relevant EU regulations on metal finishing include:

- End-of-Life Vehicle (ELV) – restricts the use of lead, mercury, cadmium and hexavalent chromium on new vehicles [A4];
- Waste Electrical and Electronic Equipment (WEEE) – requires producers of a wide range of products to severely restrain disposal of potentially hazardous materials and maximize recycling of affected consumer and industrial goods [A5]; and
- Restriction on the Use of Hazardous Substances (RoHS) – restricts, as of July 1, 2006, the placing on the EU market of new electrical and electronic equipment containing more than certain levels of six banned substances: lead, mercury, cadmium, hexavalent chromium, Poly-Brominated Biphenyls (PBB) or Polybrominated Diphenyl Ethers (PBDE) [A6].

23.2.4 Other Countries

Other countries are also introducing regulations similar to those in Europe. The Chinese and Korean policies are modeled on the EU rules, such as RoHS, with the same restricted materials.

There are other EU and international agreements and initiatives relevant to metal finishing such as the Stockholm Convention on Persistent Organic Pollutants (POPS) [A7], and the Convention on Long Range Transboundary Air Pollution (LRTAP) that includes Heavy Metals Protocols [A8]. Future actions under these agreements may force regulatory limitations on other materials, beyond the existing regulations on cadmium and hexavalent chromium.

23.3 CADMIUM ALTERNATIVES

The purpose of this section is to identify and briefly discuss existing alternative coatings to Electro-Deposited (ED) cadmium. A number of reference papers have already covered various aspects of this topic [12]-[21] and [22]; therefore, the present review will not attempt to discuss all the cadmium alternatives that have ever been proposed. Instead, it focuses on coatings that provide sacrificial corrosion protection for steels, coatings that are commercially available, and coatings that are environmentally acceptable. The requirement for sacrificial protection limits the range of candidate materials that could replace cadmium to aluminum and zinc and their alloys. Figure 23-1 presents anodic part of the galvanic series (data from http://www.corrosionsource.com/handbook/galv_series.htm) showing materials that are more electronegative than low alloy steels. When in contact, more electronegative material will act as an anode and will corrode preferentially.

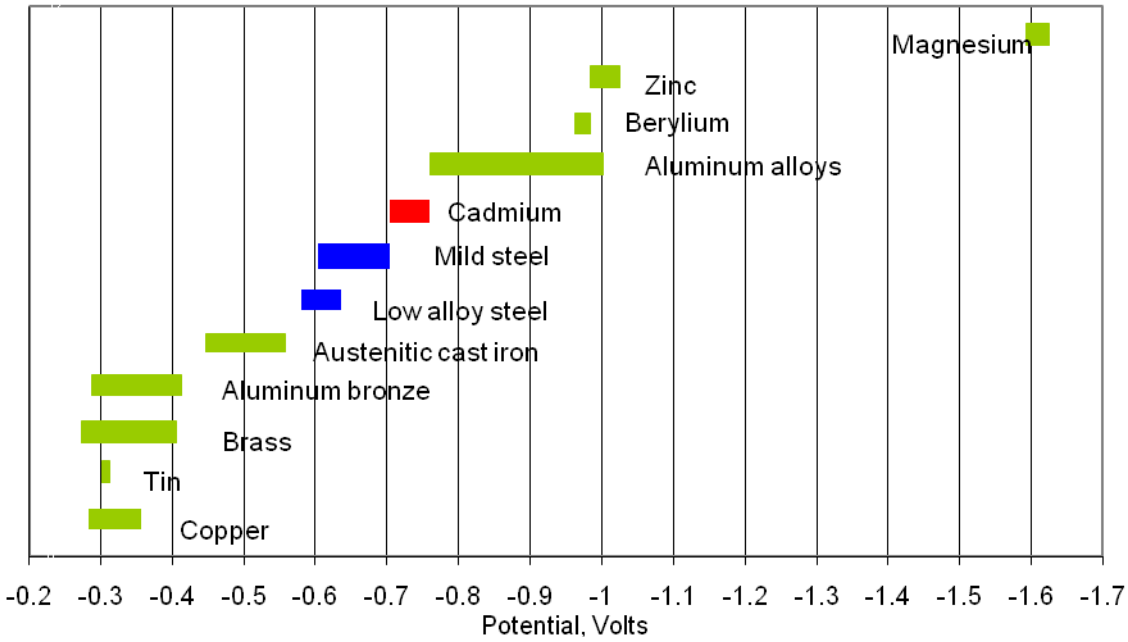

Figure 23-1: Corrosion Potentials of Selected Metals in Reference to Saturated Calomel Electrode.

The second requirement is basically about logistics, as discussed previously. The requirement for green alternatives is sometimes difficult to meet as some new materials require additional treatments that very often involve hexavalent chromium (Cr(VI)) or contain metals such as nickel or cobalt that will most likely be targeted by future environmental legislations.

Besides sacrificial corrosion properties, important technical factors in the selection of cadmium replacement coatings are:

a) Deposition temperature when applicable to high-strength steel substrates;

b) The ability to coat external and internal surfaces; and

c) The ability to produce functional coatings with thickness between 5 and 25 µm, corresponding to cadmium thickness classes specified by the ASTM Standard B 766.

The full range of tests required to qualify cadmium alternatives can be quite extensive and vary depending on coating application. The latter may include corrosion protection, lubricity for threaded hardware, electrical conductivity, and any combination of them. In the U.S.A., a test protocol was developed by the Joint Group on Pollution Prevention to validate candidate coatings [23]. A similar set of evaluation criteria was adopted in Canada [6]. Under this approach, candidate cadmium alternatives are tested under 11 general criteria to examine coating performance for all potential areas of application. Coatings that pass this screening can be further tested to produce a complete application-specific performance database. The evaluation tests proposed in the Canadian report were as follows [6]:

1) Corrosion resistance in neutral salt spray per ASTM B117 [A9].

2) Corrosion resistance in natural marine atmosphere or SO_2 salt per ASTM G85 [A10].

3) Coating adhesion under bend-to-break test per QQ-P-416 [A11].

4) Hydrogen embrittlement test per ASTM F519 [A12].

5) Fatigue of substrate test per ASTM E466 [A13].

6) Repairability: after repair, coating must pass corrosion and adhesion tests.

7) Lubricity: torque-tension characteristics.

8) Paint adhesion assessed by Plastic Media Blasting (PMB) stripping time.

9) Galvanic compatibility with aluminum alloys.

10) Compatibility with aerospace fluids such as fuels, oils and greases, and hydraulic and de-icing fluids.

11) Electrical contact resistance.

The present review covers three main groups of cadmium alternative coatings:

a) Electro-deposited zinc and aluminum alloys;

b) Vacuum-deposited aluminum and aluminum alloys; and

c) Spray-deposited aluminum and metallic-ceramic coatings.

In addition, alternative materials to replace cadmium-plated steels on the whole are also briefly reviewed. All discussed alternative technologies and coatings are presented in Figure 23-2.

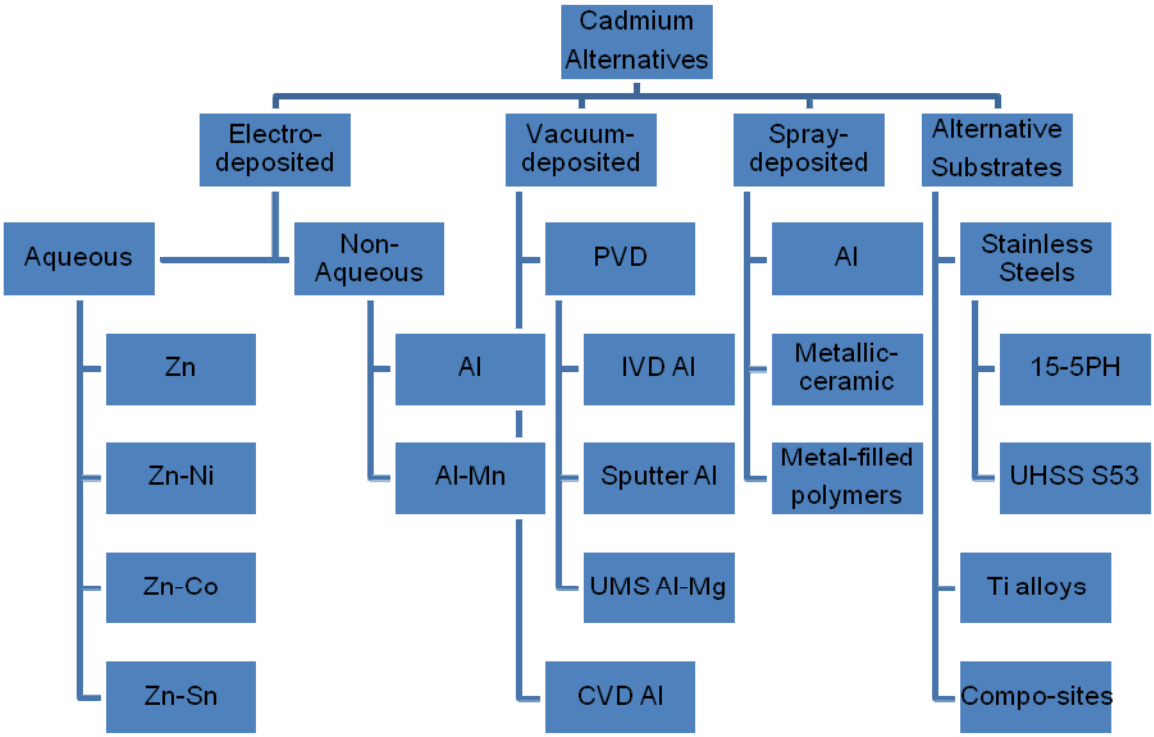

Figure 23-2: Cadmium Alternative Coatings and Materials.

23.3.1 ED Zinc-Based Coatings

Electro-deposited zinc, thanks to its general corrosion-protection properties, is the obvious choice to replace cadmium coatings on steels in many non-aerospace applications. In certain industrial atmospheres (particularly with SO_2 and CO_2), zinc performance is superior to that of cadmium [16]. However, plain zinc coatings perform rather poorly in neutral salt fog tests (less than 100 hrs to red rust) and require greater thickness plus a conversion coating in order to enhance the corrosion performance to an acceptable level. A potential problem for fasteners is the large volume of corrosion product formed and lack of galvanic compatibility with aluminum alloys [3],[15]. The latter is a common problem for all zinc alloys. Another issue is high risk of hydrogen embrittlement, thus zinc coatings are usually limited to low strength steel components.

Better performing alternatives are alloys from the zinc-nickel (Zn-Ni) system that is widely used in automotive and aerospace applications. These alloys are deposited from cyanide-free baths, which can be acid, neutral or alkaline. The acid Zn-Ni deposition process was developed by among others the Boeing Company and there are two aerospace process specifications for this alloy: BAC 5637 and AMS 2417. The acid baths produce nickel content from 10 to 14%, while alkaline baths yield about 6 to 9% Ni. In general, the acid baths produce coatings with better corrosion resistance and are more efficient that those from alkaline baths, so the risk of hydrogen embrittlement is less severe. Still, Zn-Ni coating applications in aerospace are limited to low strength steel components. The potential problem with these alloys is the need for conversion coatings (chromating of Zn-Ni alloys suppresses the dezincification process and improves the coatings' corrosion properties) and uncertain future as to the new regulations limiting the usage of nickel or some of its compounds.

Alloys of the zinc-cobalt (Zn-Co) system, like these of the zinc-nickel system, were developed to meet requirements of the automotive industry. The optimum cobalt concentration in zinc-cobalt alloys is

thought to be in the range 4 – 8 %, but for commercial reasons the level of cobalt is usually between 0.6 and 1.2 % [14]. In various tests zinc-cobalt coatings demonstrated corrosion resistance equivalent to that of cadmium [14],[16],[24]. With some topcoats Zn-Co coatings can have torque-tension characteristics comparable to that of cadmium [25]. Unfortunately, as with nickel, the future use of cobalt is uncertain due to incoming environmental regulations.

Tin-zinc (Sn-Zn) coatings were developed as a direct replacement for cadmium. They offer all the advantages of cadmium like high resistance to corrosion, lubricity, solderability and good electrical conductivity, but they do not have the toxicity of cadmium, although some deposition processes utilize cyanide baths. Compositions range from 10% Sn to 85% Sn with balance Zn, but the most common compositions are between 70% and 80% Sn. Tin-zinc can be deposited from acid, alkaline, or neutral baths, however all processes are expensive since the tin-zinc anodes must be specially cast. As is the case with all zinc alloys, tin-zinc also requires chromate (or alternative) conversion coating for best performance. Tin-zinc coatings with 70% Sn have good solderability and do not grow “whiskers” or dendritic crystals for periods up to 600 days, making them good cadmium alternatives for electrical connectors. Additionally, galvanic compatibility of tin-zinc coatings with aluminum alloys is satisfactory, and they can be applied to steel fasteners for use on aluminum alloy panels [26].

23.3.2 ED Aluminum-Based Coatings

Aluminum or aluminum alloys can be electro-deposited only from non-aqueous electrolytes. The Siemens Galvano Aluminum process (SIGAL) for deposition of pure aluminum has been known for years, but was only recently developed to the production level by AlumiPlate Inc of Minneapolis, and marketed as a new alternative for cadmium. ED aluminum from the AlumiPlate process has been found to be technically superior to other alternatives in various tests including corrosion resistance (also G85 SO2 salt fog test), hydrogen embrittlement, and electrical conductivity. This coating is already used on a small number of military aircraft components, and has recently been qualified for F-22 landing gear components [12]. In addition, the AlumiPlate process is used on some connectors produced by Amphenol. However, the AlumiPlate process is currently available only from a single source and the process itself is very difficult to work, since it involves the use of pyrophoric aluminum compounds and flammable organic solvents such as toluene. Consequently, the plating process must be done in a sealed tank, with inert gas over the plating bath and a load-lock used to maintain an oxygen-free and water-free atmosphere.

Aluminum-manganese (Al-Mn) is a non-aqueous ED coating currently in development [12],[27]. The alloy composition is usually 13 – 25 % Mn and the process itself is quite complex, and involves molten salt baths and inert atmospheres (typically dry nitrogen). Initial results show that the Al-13Mn survived a salt spray corrosion test for 3,000 hrs with no rust, while scribed material lasted 1,000 hrs indicating good sacrificial properties. Comparing to pure aluminum, Al-Mn alloys are less electronegative, thus should have lower corrosion rates. In addition, the chemistry of the Al-Mn molten salt bath coatings is practically independent of current density, which should make it possible to plate complex shapes reproducibly. However, this process is not at the production level as yet [27].

23.3.3 Vacuum-Deposited Aluminum and Aluminum Alloys

Aluminum coatings can be very effectively deposited by Physical or Chemical Vapor Deposition (PVD or CVD) methods. Since the deposition takes place in vacuum, the risk of hydrogen embrittlement is virtually eliminated and the process is environmentally clean. The main drawbacks of PVD processes are:

a) The limited ability to coat internal diameters owing to the line-of-sight nature of the process;

b) Relatively low deposition rates; and

c) The high investment cost.

The CVD process is more flexible in terms of coating small ratio internal passages, but usually the deposition temperatures are too high for high strength steels.

The Ion Vapor Deposition (IVD) process to produce aluminum coatings involves bombarding the substrate with an ionized aluminum vapor in vacuum. This process was first used by McDonnel Douglas Aircraft (now Boeing) and has been commercially available for many years. It is also recognized as a viable alternative to cadmium plating by MIL-C-83488. The IVD Al coatings show good substrate adhesion but they tend to be porous and coated components require glass-bead peening and chromating. Corrosion properties of IVD Al are good, although poorer than those of cadmium, but hydrogen embrittlement is eliminated and the effect on substrate fatigue is negligible. Obviously, IVD Al coatings on threaded hardware require dry film lubricants or equivalent top coats. The main obstacle to the wide use of IVD Al process seems to be the high cost of deposition.

Pure aluminum coatings applied by sputtering, including Unbalanced Magnetron Sputtering (UMS), offer several advantages over the IVD deposited coatings: higher density, a non-columnar structure (no need for post-deposition peening), better thickness control, and higher coating uniformity. Because of higher density, UMS Al coatings have better corrosion properties compared to IVD Al. Since the source (target) materials are not melted during the UMS process, co-deposition of dissimilar materials such as for example aluminum and magnesium or aluminum and molybdenum is possible in multi-target arrangements. Several aluminum alloys have been tried as cadmium alternatives, including aluminum magnesium (Al-Mg), aluminum molybdenum (Al-Mo), aluminum titanium (Al-Ti) and aluminum zinc (Al-Zn) [6],[14],[28]-[34] and [35]. However, none of these materials have been developed beyond the research level.

Other production coatings in the group of vacuum technologies are sputtered pure Al (plug-and-coat system developed by Marshall Labs) used for internal diameters of big landing gear components [12], and low temperature CVD Al from the LOM™ process by Liburdi [36]. The Liburdi process is used to apply a high purity aluminum coating over the exterior and internal surfaces of turbine blades. However, little information is available on the coating performance, except that it passed 600 hrs B117 (salt spray) corrosion test, thus qualifying for automotive use. Since the deposition temperature is above 260°C (500°F), CVD Al cannot be applied to many structural alloys used in aerospace [12].

23.3.4 Spray Deposited Cadmium Alternatives

There are several different aluminum-based coatings that can be deposited by spraying: aluminum and Al alloys, metallic-ceramic coatings, and Al- and Zn-filled polymers [12].

Thermal spray (flame or arc) is a very flexible and cost-effective process for deposition of pure Al, Al-Mg and Al-Zn alloys on bigger components and large structures such as bridges or communication towers where relatively high thickness (above ~75 µm or 0.003”), surface roughness and inability to coat small internal diameters (below ~ 7.5 cm or 3”) are not problems. Wire arc spray of Al and Al alloys is specified for use on some landing gear and other aircraft components (e.g., the Bombardier Dash-8 turboprop) [12]. For this type of application the spray gun can be controlled by an industrial robot to ensure uniformity and repeatability.

Metallic-ceramic coatings are a class of spray-deposited coatings consisting of metal particles (usually aluminum powder or zinc flakes) in an inorganic (usually chromate-phosphate binder) matrix [12],[18],[33]. These coatings are sprayed as slurry and subsequently cured at temperatures above 200°C. Due to the presence of the active metal particles, metallic-ceramic coatings provide good sacrificial protection for ferrous alloys. They are widely used by the aerospace sector in gas turbine applications and also as alternatives to cadmium in some applications. However, the latter appear to be problematic because of hydrogen embrittlement issues, minimum coating thickness (above 50 µm), curing temperature for some

formulations, and common use of chromate conversion coatings [12]. Two known North American suppliers of metallic-ceramic coatings are Sermatech of Limerick, PA (Serme Tel series of coatings) and Coating for Industry of Souderton, PA (AlSEAL coatings).

Metal-filled polymer coatings are widely used to provide corrosion resistance and proper torque-tension to fasteners in the automotive industry. These coatings are usually deposited either by spraying or by dip-spinning. There is a very wide variety of proprietary and non-proprietary polymer coatings that incorporate metal flakes or powders for corrosion resistance. Most commonly, the material is an epoxy with aluminum or zinc filler and a fluoropolymer (PTFE or similar) topcoat for lubricity. The methods and materials involved are commercially available and inexpensive. However, thickness control is limited and coatings require curing at temperatures up to 218°C. Applications in the aerospace industry may require tougher process control to ensure repeatability of coating properties.

23.3.5 Alternative Substrate Materials

One way to eliminate cadmium (and alternative coatings) altogether is by replacing coated steel components by corrosion resistant materials such as titanium alloys, stainless steel or composites. This is already occurring in the aerospace industry (e.g., the Boeing 787 is in large part composite, with many Ti alloy structural members) and the use of stainless steel is now standard for aircraft actuator housings and GTE fasteners [13]. Material substitution, mostly in the form of corrosion-resistant alloys, is the most common and successful approach. Most aerospace actuator rods and outer cylinders are now made from 15-5PH stainless steel rather than the older 4340 high strength steel that required cadmium plating for corrosion resistance. A new ultra high strength stainless steel, such as S53, has been recently developed and is currently being validated [13]. This steel has mechanical properties equivalent to 300 M landing gear steel (UTS = 280 ksi) and corrosion resistance similar to 15-5PH stainless steels. Note, however, that galvanic corrosion between aluminum structures and steel fasteners is still an issue for the new stainless steels. However, replacement of Al alloys by composites in aircraft fuselage solves, at least in part, the compatibility problem.

23.3.6 Summary on Cadmium Alternatives

Table 23-1 presents all discussed coatings and compares them against general requirements for cadmium alternatives. As a reference, electro-deposited cadmium features are listed as well. It is evident from the Table 23-1 that most electro-deposited coatings appear to be straightforward and non-expensive replacements for cadmium, except for ED Al and Al-Mn that are expensive and not widely available. However, the biggest problem for the ED Zn alloys is common use of conversion coatings containing hexavalent chromium. Vacuum-based PVD-UMS and CVD coatings do not have this problem, but these technologies are expensive and not widely available. The last group of spray deposited materials is very economical, but relatively large coating thickness put them out of the range for most cadmium applications. Besides, similarly to PVD processes, they are line-of-sight deposition techniques, with limited capabilities to coat Internal Diameter (ID) surfaces.

Table 23-1: General Requirements for Cadmium Alternative Coatings.

Requirement → Coating ↓	Low Dep. Temperature	OD/ID Coverage	Thickness 5 – 25 µm	Low Cost	Wide Availability	Environmental Issues
ED Zn	P	P	P	P	P	Cr(VI)
ED Zn-Ni acid	P	P	P	P	P	Cr(VI), Ni
ED Zn-Ni alkaline	P	P	P	P	P	Cr(VI), Ni
ED Zn-Co	P	P	P	P	P	Cr(VI)
ED Zn-Sn	P	P	P	?	P	Cr(VI)
ED Al	P	P	P	F	F	Toluene
ED Al-Mn	F	P	P	F	F	Wastes, fumes
IVD Al	P	F	P	F	P	Cr(VI)
Sputtered Al	P	P/F	P	F	F	None
UMS Al-Mg	P	F	P	F	F	None
CVD Al	F	P	P	?	F	Metal organics
Th. sprayed Al	P	F	F	P	P	None
Met-ceramic	P/F	?	F	P	P	Cr(VI)
Met-filled polymer	P	?	F	P	P	None
ED cadmium	P	P	P	P	F	Cd, cyanides, Cr(VI)

Legend: P = pass

F = fail

P/F = result depends on actual version/method, etc.

? = not enough data

Cr(VI) = may contain hexavalent chromium

Ni = contain toxic nickel compounds

Table 23-2 presents key technical requirements for discussed cadmium alternative coatings in comparison with cadmium performance. The technical requirements are related to main areas of application and based on evaluation criteria discussed in Section 23.3.

Table 23-2: Key Technical Requirements for Cadmium Alternative Coatings.

Requirement → Coating ↓	Corrosion				Hydrogen Embrittlement	Fatigue Debit	Lubricity	Compatibility with Al Alloys	Electrical Conductivity
	Salt Spray B117								
	un	sc	SO_2	mar					
ED Zn	F	–	P	Pc	F	P	F	F	–
ED Zn-Ni acid	P	P	F	Pc	?	F	Pc	F	–
ED Zn-Ni alkaline	P	F	F	Pc	?	?	Pc	F	–
ED Zn-Co	Pc	–	–	–	–	–	Pc	F	–
ED Zn-Sn	P	–	F	–	?	P	P	P	P
ED Al	P	–	P	–	P	–	F	P	P
ED Al-Mn	P	P	P	–	P	P	P	P	–
IVD Al	Pc	Pc	Pc	–	P	P	Pc	P	Pc
Sputtered Al	P	P	P	–	P	P	Pc	P	–
UMS Al-Mg	P	–	–	P	P	–	Pc	F	–
CVD Al	F	–	–	–	P	P	F	P	–
Th. sprayed Al	–	–	–	–	P	P	–	P	–
Met-ceramic	P	F	P	–	?	?	F	–	–
Met-filled polymer	–	–	–	–	P	–	P	P	-–
ED cadmium	Pc	Pc	F	Pc	Pb	P	Pc	P	Pc

Legend:
P = pass
Pc = pass if top-coated or conversion-coated
Pb = pass if baked out
F = fail
– = not applicable or no data
? = not enough data
un = unscribed condition
sc = scribed condition
mar = marine environment

The technical performance of electro-deposited alternatives appear to be satisfactory, however these coatings require additional treatments to improve their corrosion resistance or lubricity. In addition, the big problem for the ED Zn alloys is hydrogen embrittlement and lack of galvanic compatibility with Al alloys. Electro-deposited Al and Al-Mn have better corrosion resistance and no embrittlement problem, but similarly to other Al based coatings (except metal-filled polymers) have poor lubricity. It is also noticeable that only few alternatives are electrically conductive, thus more development in this area is needed. Most alternative coatings have acceptable fatigue debit. Since corrosion performance and hydrogen embrittlement are the

most critical performance criteria for cadmium alternatives in aerospace, aluminum based coatings appear to be preferred choice in a long run; in particular, IVD Al for big parts and external surfaces, and ED Al for small complex parts and internal diameters.

23.4 HARD CHROMIUM ALTERNATIVES

Industrial hard chromium, also known as hard chrome, is one of the most extensively used electroplated coatings in the aerospace and automotive industries [7],[13],[37] and [38]. It is used by original equipment manufacturers for wear and corrosion protection and to a lesser extent for aesthetics, and by repair and overhaul facilities to rebuilding worn parts. In the aerospace industry, the typical applications include landing gear components, hydraulic actuators, turbine engine shafts, bearings, and propeller hubs. In automotive, crankshafts, valves, hydraulic components, piston rings, and cylinder linings are typical applications. Military agencies are using hard chrome extensively for protection of inside bores of gun barrels. The main issues affecting usage of chromium plating are process toxicity (presence of hexavalent chromium Cr(VI)), low plating bath efficiency (around 15%) that leads to high energy consumption, the presence of cracks causing inconsistent corrosion performance, thickness uniformity and the necessity of post-treatment machining, and hydrogen embrittlement in steel substrates requiring post-deposition bakeout. Hard chromium alternatives are expected not only to match the chromium performance in given applications, but also address these issues with a view to gaining some improvement. All discussed here alternative technologies and coatings are presented in Figure 23-3.

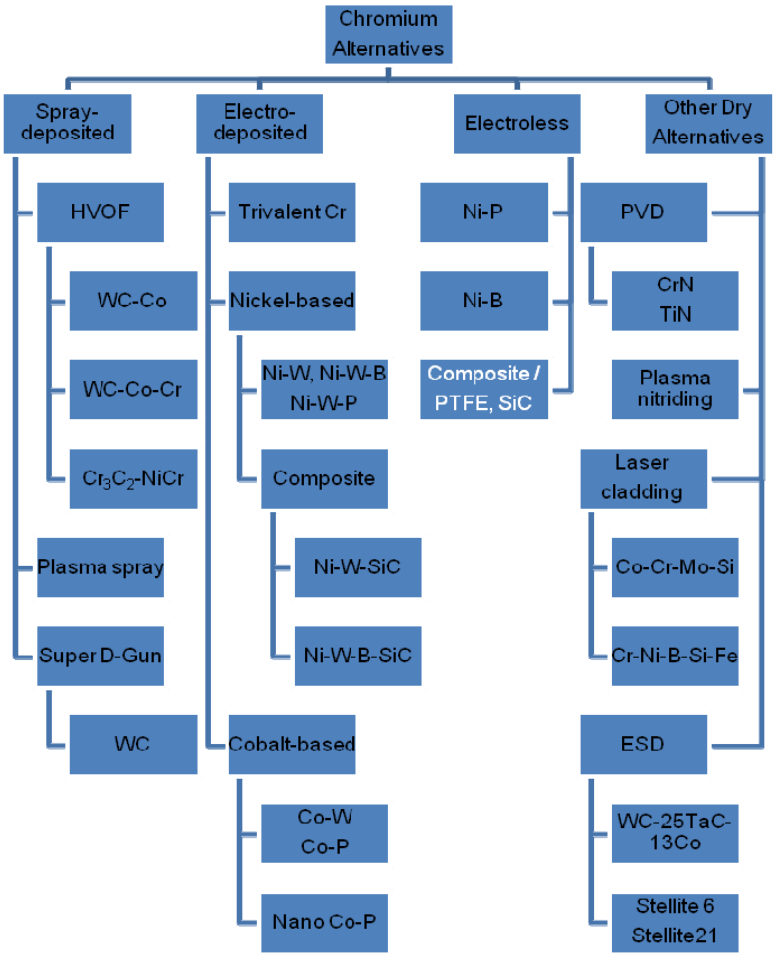

Figure 23-3: Chromium Alternative Coatings.

23.4.1 Spray Deposited Hard Chromium Alternatives

Thermal spraying is widely used in aerospace and many other industries for deposition of high quality metallic, ceramic and ceramic-metal composite coatings. There are three basic spraying technologies available as alternative technologies to hard chromium plating.

The leading technology among hard chromium alternatives is the High Velocity Oxygen Fuel (HVOF) spraying of cermets. This technology is versatile, environmentally benign, and cost effective. The coatings are most often cermets containing WC-Co, WC-Co-Cr and Cr_3C_2-NiCr, and have been found to have physical properties equal to or better than those of hard chromium. In fact, the service temperature of typical cermets can be up to 815°C (1500°F), which is double the hard chromium capability. Deposition is completed by propelling the coating with a high velocity and high temperature flame produced through the combustion of oxygen and fuel. A significant advantage of this technology is the high deposition rate. Disadvantages include the inability to coat small and intricate parts, or parts with a small internal diameter (about 100 mm or 4”). In addition, machining is required after coating deposition due to the surface roughness and typical over-spraying. The aerospace industry has targeted the use of HVOF coatings for landing gears, flap actuators, shafts, hub propellers, and hydraulic parts [13],[37]. Other applications include industrial hydraulic and pneumatic actuators, and mill rolls used in steel, paper and plastic industries.

Plasma spraying is used to deposit similar materials and has similar applications to HVOF. However, thanks to the smaller size of the plasma gun and short standoff distance, it can be used to coat Internal Diameters (ID) not accessible to HVOF [13],[38]. Presently, the minimum ID is about 40 mm (1.6”) in the case of the specially developed F-300 plasma gun from Sulzer Metco [38].

The detonation gun thermal spray process was originally developed by the Union Carbide Corporation and is now available from Praxair Surface Technologies under the name of D-Gun and Super D-Gun [39],[40]. In this technique, the powder particles suspended in the flammable gas mixture are accelerated by a detonation ignited by spark plug at the rate up to 8.6 times per second. The repeated detonation cycle produces a coating on the substrate placed 50 – 100 mm from the barrel. Super D-Gun process yields excellent coating properties particularly for tungsten carbides coatings. Bond strength is reported to reach 210 MPa (about twice the corresponding value for plasma spraying) and the coating porosity is below 1%. However, detonation gun process is strictly line-of-sight and more expensive than the other thermal spraying techniques.

23.4.2 Electrolytic Hard Chromium Alternatives

Wet technologies such as trivalent chromium and nickel depositions are in use mostly for ID applications where line-of-sight spray technologies fall short. The strong point of these processes is that the plating is well established within the industry and there is a network of suppliers and plating shops willing to adapt to the new environmental standards. The weakest point, common for all wet technologies, is the volume of wastes generated.

Electro-deposited trivalent chromium, obtained from Cr(III)-based electrolytes, is environmentally sound technology; however, physical and chemical properties of the coatings are still inferior to hexavalent hard chrome, despite years of effort [7],[13]. For now, trivalent chromium applications are limited to thin decorative coatings. Thicker coatings are suitable only for simple substrate configurations.

Electroless nickel and nickel alloys, despite all environmental concerns are still used as hard chromium alternatives. Electroless nickel-phosphorus (Ni-P) is a hardenable, corrosion resistant coating consisting of nickel alloyed with a varying percentage of phosphorous (usually 8% to 10%). It offers good thickness uniformity and control. The coating properties are largely determined by coating composition, with 8% phosphorus coating being harder and 10% phosphorus coating being more corrosion resistant. Electroless

Ni-P composite coatings are available with additions such as Silicon Carbide (SiC) for wear resistance or teflon (PTFE) for lubricity. Thanks to the ability to cover parts of complex geometry, typical applications of electroless Ni-P include hydraulic valves, pump components, moulding dies and fuel injector plates. Electroless nickel-boron (Ni-B) coating exhibits better wear resistance, lower friction, higher hardness but lower corrosion resistance compared to hard chrome. In addition, Ni-B coatings are expensive to produce, not widely available and plating bath contains lead or thallium that are toxic materials. Typical areas of application include jet engine components, glass manufacturing, foundry molds, gears, shafts, knife blades and drills.

There are a number of electroplated alloys considered as drop-in replacements for hard chromium [7],[13]. They are based either on nickel (Ni-W, Ni-W-B, Ni-W-P, Ni-W-SiC and Ni-W-B-SiC) or cobalt (Co-W and Co-P). However, nickel (or some of it compounds) already faces increased environmental scrutiny and cobalt's future is also uncertain. To complicate things even further, cobalt is more expensive than nickel. Nevertheless, worth mentioning here is nanocrystalline Cobalt-Phosphorus (Co-P) coating recently developed by Integran Technologies [41]. Thanks to better microstructure and low residual stress, the nanocrystalline Co-P coatings are more corrosion resistant than hard chromium. The process is not embrittling, although the fatigue effect on the substrate is not known. In general, electroplated alloys surpass hard chromium in many respects and may be used in selected applications as a direct replacement. However, environmental restrictions (nickel compounds in plating bath) and problems with process control (e.g., SiC particles in composite coatings) may limit or even eliminate their application in the future.

23.4.3 Other "Dry" Alternatives

In principle, any hard coating can be considered as a hard chromium alternative [7]-[9] and [43]. The candidate "dry" alternatives can be deposited by vacuum-based PVD methods, laser techniques, and micro-welding. In addition, surface modifications that do not create coatings but improve surface properties, such as ion implantation, plasma nitriding and thermo-chemical treatment, can also be considered. The techniques that have been considered as hard chromium replacement are discussed next. However, comparing to spray technologies and plating, they have only niche applications.

PVD deposition techniques are relatively well-known alternatives for hard chromium plating. Included in this category are sputtering and cathodic arc deposition that produce thin coatings (below 10 µm), and Electron Beam-PVD (EB-PVD) techniques which can produce coatings up to hundreds of µm in thickness. Two of the most important features of PVD coatings, relevant to hard chromium applications, are the high deposition rate and compressive residual stresses in the coatings after deposition. The high deposition rate of EB-PVD allows for significant thickness build-up and can be used for refurbishment purposes as well as for net shape forming [42]. The compressive residual stresses, characteristic of all PVD coatings, improve the corrosion resistance of the coating. A variation of PVD technique, Ion-Beam Assisted Deposition (IBAD), is a combination of low energy ion bombardment and a physical vapor deposition. This process produces high-density coatings with excellent adhesion and controllable residual stresses. Among PVD coatings considered as hard chromium alternative are CrN, TiN and Metal containing Diamond-Like Carbon (Me-DLC) coatings that can be deposited by magnetron sputtering or cathodic arc evaporation [43]. Overall, PVD methods are environmentally clean and offer high quality coatings. Although the capital cost for PVD equipment can be high, this can be offset by mass production.

Ion technologies such as ion implantation or plasma nitriding use energetic ion bombardment to modify surface properties of the material [7]. Since no coating is produced, there is no change to part dimensions, no problems with adhesion, and residual stresses are negligible. One of the newest developments, Plasma Source Implantation is a low-cost and non-line-of-sight technique, most often used for nitriding. So-called plasma nitriding can be used in combination with physical vapor deposition or electro-deposition. For those parts that already have hard chromium coating plated, the application of nitriding leads to the

formation of CrN phases on the surface. This increases the wear resistance and service life of chromium coated parts. Although not the ideal solution, ion technologies can provide a versatile means to enhance chromium coatings already in use and thus contribute to the lower life cycle cost of coated parts. The latter translates into longer times between refurbishments, resulting in less environmental impact.

Laser Cladding (LC), which is also known as laser plating or hard facing, is another technology with potential as a chromium plating alternative [44],[45]. The cladding process consists of melting the coating, which is usually in the powder form, together with the surface layer of the substrate. The coefficient of mixing is usually 0.1 indicating that there is little mixing with the substrate. LC produces a strong metallurgical bond and preserves the unique properties of the coating material and the substrate. Among the varieties of materials used, Co-Cr-Mo-Si and Cr-Ni-B-Si-Fe compositions are known to provide good combinations of wear and corrosion resistance. In comparison to hard chromium, the advantages of cladding processes include: absence of micro-cracking, low energy consumption, low heat input, and coating composition flexibility. Similar to chromium plating, post-deposition machining is required.

Electro-Spark Deposition (ESD) is in principle a pulsed-arc micro-welding process that uses short duration, high current electrical pulses to deposit, with very low heat input, a consumable electrode material on a metallic substrate [46],[47]. The process is environmentally benign, cost-effective and requires no special chambers, or operator protection. This commercially available technology offers a wide selection of coating materials, and portability of coating equipment. In addition, ESD can be applied to inside diameters as small as 7.6 mm (0.30”). In principle, any electrically conductive material can be deposited, but for the purpose of hard chromium replacement, tungsten carbides such as WC-25TaC-13Co, and cobalt-base alloys such as Stellite 6 and Stellite 21 have been successfully used. Characterization of the ESD coatings showed that compared to hard chromium, the ESD coatings have comparable corrosion performance, and slightly lower hardness and wear resistance. Fatigue testing, however, revealed that in the case of high-strength steel substrates (e.g., 4340) the loss of fatigue life could reach 20%. The low deposition rates may also be a concern, but ESD can play a significant role in on-site repairs of original materials and chromium coatings.

23.4.4 Summary on Hard Chromium Alternatives

Table 23-3 and Table 23-4 present all discussed alternative coatings and compare them against relevant properties of Electro-deposited Hard Chromium (EHC). Since deposition temperature and service temperature are not problematic for alternatives considered in this review, they are not listed in Table 23-3 as a requirement.

Table 23-3: General Requirements for Hard Chromium Alternative Processes and Coatings.

Requirement → Process/Coating ↓	Low Cost	Rebuild Capacity	Post-Deposition Machining	ID Coverage (min dia)	Environment Issues	Availability and Fit with OEM/MRO
EHC	Yes	Yes	Needed	Yes	Cr(VI)	Yes
HVOF WC-Co WC-Co-Cr Cr_3C_2-NiCr	P	P	P	100 mm	?	P
Plasma spray	P	P	P	40 mm	None	P
Super D-gun	F	P	P	F	None	F
ED trivalent Cr	P	F	None	P	None	?
Electroless Ni-P	P	P	?	P	Ni	P
Electroless Ni-B	F	P	?	P	Ni, Tl, Pb	P
Electroless Ni-P-SiC	P	P	?	P	Ni, SiC	P
ED Ni-W	P	P	?	P	Ni	P
ED Ni-W-B	P	P	?	P	Ni	P
ED Ni-W-P	P	P	?	P	Ni	P
ED Ni-W-SiC	P	P	?	P	Ni, SiC	P
ED Ni-W-B-SiC	P	P	?	P	Ni, SiC	P
ED Co-W	F	P	?	P	None	P
ED Co-P	F	P	?	P	None	P
ED nano Co-P	F	P	?	P	None	?
PVD CrN	F	F	None	F	None	F
PVD TiN	F	F	None	F	None	F
PVD Me-DLC	F	F	None	F	None	F
Plasma nitriding	P	F	None	P	None	P
LC Co-Cr-Mo-Si Cr-Ni-B-Si-Fe	P	P	P	F	None	F
ESD WC-TaC-Co Stellite 21	P	P	P	7.6 mm	None	P

Legend: P = pass (same as EHC or better)

F = fail

? = not enough data

OEM/MRO = Original Equipment Manufacturer / Maintenance Repair and Overhaul facility

Table 23-4: Technical Requirements for Hard Chromium Alternative Processes and Coatings.

Requirement → Process/Coating ↓	Hardness HV	Wear Resistance	COF	Corrosion Resistance	Hydrogen Embrittlement	Fatigue Debit
EHC	800 – 1000	High	0.12	F (cracks)	Needs bake out	F
HVOF WC-Co	P	P	–	?	P	?
WC-Co-Cr	P	P	–	P	P	?
Cr_3C_2-NiCr	P	P	–	P	P	–
Plasma spray	P	P	–	P	P	P
Super D-gun	P	P	–	P	P	P
ED trivalent Cr	F	F	–	?	–	–
Electroless Ni-P	P	P	–	P	–	–
Electroless Ni-B	P	P	P	F	–	–
Electroless Ni-P-SiC	P	P	–	P	–	–
ED Ni-W	P	P	P	P	–	–
ED Ni-W-B	P	P	P	–	P	F
ED Ni-W-P	P	P	–	P	–	–
ED Ni-W-SiC	P	P	–	–	–	P
ED Ni-W-B-SiC	P	P	–	–	–	P
ED Co-W	F	P	–	P	–	–
ED Co-P	P	P	–	–	–	–
ED nano Co-P	P	F	F	P	P	?
PVD CrN	P	P	F	P	P	P
PVD TiN	P	P	F	P	P	P
PVD Me-DLC	P	P	P	P	P	P
Plasma nitriding	P	P	–	–	P	P
LC Co-Cr-Mo-Si	P	P	–	P	P	P
Cr-Ni-B-Si-Fe						
ESD WC-TaC-Co	P	P	–	P	P	P
Stellite 21	F	F	–	P	P	F

Legend: P = pass (same as EHC or better)

F = fail

? = not enough data

– = not applicable or no data

As evident from Table 23-3, all thermal spray processes and laser cladding have proven rebuilding capabilities, and as a consequence, post-deposition machining is typically required. It is also noticeable that most of "wet" ED and Electroless coatings have variety of potential environmental problems, the most serious in the case of Electroless Ni-B, relating to nickel, lead (Pb) and thallium (Tl) contents. In addition, all composite coatings have problems with air emission of SiC particles. On the other hand, all wet coatings have good OD/ID coverage. This property is lacking from the "dry" alternatives, where PVD, LC and Super D-Gun technologies are strictly line-of-sight, while HVOF and plasma spraying have quite serious limitations as to minimum diameter that could be coated. The PVD and laser technologies are not widely available at service depots and PVD in particular can be expensive, especially on small scale production.

With few exceptions, hard chromium alternatives have no problem with meeting the hardness and wear resistance criteria. Also the corrosion resistance is not an issue. Since hydrogen embrittlement is critical only for high-strength substrates, suitable alternative can be found for most of applications. Overall, when combining general requirements (with the low cost as a go / no go criteria) and technical requirements, the spray technologies (HVOF and Plasma) and laser cladding appear to be the best alternatives for big components and mostly external surfaces, while variety of electro-deposited and electroless coatings can be applied to coat ID's. However, future environmental restrictions concerning nickel compounds may complicate this picture, as Ni-based coatings cover most ID applications. Plasma nitriding may replace hard chromium in applications on some small and complex components, while Electro-Spark Deposition of carbides may be used for field repairs.

23.5 CONCLUSIONS

There are many potential alternatives for both hard chromium and cadmium. In the case of hard chromium, HVOF and plasma spraying of cermets has been the leading process of choice for most applications. However the electrolytic Ni-based coatings are still needed for internal surfaces. Laser cladding, plasma nitriding and Electro-Spark Deposition processes may also play a role in specific applications. In the case of cadmium, however, the situation is more complicated and serious concessions are needed. First of all, there is no leading technology, and electro-deposition of zinc- and aluminum-based alloys is competing with other techniques like PVD, CVD and thermal spray technologies. However, the big problem for the ED Zn alloys is hydrogen embrittlement and lack of galvanic compatibility with Al alloys that make most of structural component in aerospace. Electro-deposited Al and Al-Mn do not have these problems, but similarly to other Al-based coatings have poor lubricity that complicates applications to threaded hardware. Another problem is that only few cadmium alternatives are electrically conductive, thus more development in this area is needed. Since corrosion performance and hydrogen embrittlement are the most critical performance criteria for cadmium alternatives in aerospace, aluminum based coatings, despite higher cost, appear to be preferred choice in a long run; in particular, IVD Al for big parts and external surfaces, and ED Al for small complex parts and internal diameters. Sputtered Al may also find niche applications. In other areas than aerospace, selection of suitable cadmium alternative appears to be not that critical.

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