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Restrictions on the Use Cadmium Coating in Industries

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ABSTRACT

Cadmium electrochemistry coatings on carbon steel have strong corrosion resistance, especially in marine environments, low friction coefficient and afford a good electrical contact. They are used by the petroleum, automotive, electric and electronic industries and moreover in locks production. In Brazil, due to their good performance in salty environments, these coatings are still widely used. However, its use diverse, before his toxicity not propagated and the low melting point may result in restrictions on some industries like food and pharmaceuticals. Cadmium is regarded today as one of the largest metal toxicity. According to surveys conducted in 2005 by American agencies ATSDR (Agency for Toxic Substances and Disease Registry) and EPA (Environmental Protection Agency) cadmium occupies the 7th place in toxic substances with increased risk of harm to humans. This work aims to show the processes of cadmium coating deposition, its advantages and disadvantages, at the same time alert regarding the problems caused by cadmium in environment and the possible health problems caused by cadmium absorption.

Keywords: *cadmium, coating, corrosion, electrolytic process, environment*

1. INTRODUCTION

The history of non-ferrous metal technologies show that since the middle ages yellow residues (cadmium oxide) appeared on the chimneys of brass foundries ovens due to cadmium contaminations in the zinc slag. However, only in 1817, the element cadmium was discovered by Dr. Friedrich Strohmeyer, chemistry and pharmacy professor at Gottingen University, Germany [1].

The only cadmium mineral known is a rare ore greenockite (CdS). Found in association with zinc and lead ores and in very small quantities with many other minerals as blend (ZnS), calamine ($ZnO.SiO_2$), smithsonite ($ZnCO_3$). Due to volatility of the metal mainly produced during smelting and refining of zinc as a by-product. Cadmium is industrially obtained by the carbothermic process during zinc distillation (**$ZnO + C \rightarrow Zn_{(g)} + CO$**) or recovered during zinc electrorefining. Cadmium is a white metal with characteristic metallic brightness, soft, ductile and malleable. Cadmium is used in Ni-Cd batteries, as paints and plastics pigment, in many alloys and as electrochemistry coating.

Cadmium electrochemistry coatings have many uses because they have good corrosion resistance in saline environment, have low friction coefficient and make a fair electrical contact. Cadmium coatings are used mostly in components for the electrical, electronic, communications, automotive, aeronautic and locks industries. The future of cadmium coatings is in the hands of environmental bodies since, according to many papers, cadmium and its compounds handling is very hazardous and should be banned. It's estimated that even in small quantities and with short exposure times they are lethal.

Cases of cadmium contamination were widely reported after the Second World War. Notably the incident on the borders of Jintsu river, in the Funchu-Machi region, Japan where peasants and fishermen suffered from rheumatic pains and mialgies victims of industrial effluents of a lead and zinc processing industry nearby. That malady, caused by cadmium, a natural contaminant of the process, became known to the medical sciences as Itai-Itai according to Friberg et al [2].

Some years after that, Goodman & Gilman [3] spoke of the risks to the kidneys in case of cadmium contamination by dust, vapor or soluble salts ingestion when in concentrations in excess of 200 μg/g. In spite of that, forty years after those alerts we still have worldwide, great cadmium releases to the environment. Other contaminations for cadmium in residues of electronic components are told in Lagos, Nigeria [4].

In Brazil, Tavares [5] speaks of high cadmium concentrations in the blood of children at Santo Amaro, Bahia, probably caused by contaminations of cadmium containing solid effluents originated from a lead industry nearby. High and variable cadmium concentrations have been detected in Sepetiba bay (Rio de Janeiro), originated from effluents of a zinc refining plant located at Itaguaí (currently disabled), some 70 km from Rio de Janeiro [6]. According to Greenpeace [7] a study accomplished in Brazil showed that an area of vegetables culture using fertilizer originating from organic garbage composting, showed that cadmium values (10 mg/kg) were high. Especially considering that the World Organization of Health recommends that the maximum allowed, daily, for ingestion it is 1μg/kg, in other words, 10.000 times superior to the threshold values.

2. CADMIUM COATING PROPERTIES

The advantage principal of coating cadmium over coating zinc deposits becomes evident on corrosion testing. In direct contact with sea water and sodium chloride solutions, and also under tropical atmospheric conditions, cadmium possesses considerably greater

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chemical stability than coating zinc. In evaluations carried out with coatings of cadmium and zinc coatings in rural and marine environments the cadmium carbonates and basic chlorides which are formed are insoluble and corrosion is stifled to a greater extent than is the case with the more soluble zinc carbonates and basic chlorides, so tending toward a longer life with cadmium coatings.

In the cadmium electrodeposition process, cadmium ions (Cd^{2+}) in the bath suffer reduction by an electrical current to cadmium and are deposited at the metallic surface of a cathode (negative electrode) where as the anode (positive electrode) is generally made of rods or balls of cadmium (figure 1). The electrolytic deposition of cadmium, generally use high purity cadmium anodes [8]. The cathodic and anodic reactions referring to cadmium deposition and anode dissolution are:

- cathodic reaction : $Cd^{2+} + 2e \rightarrow Cd$;
- anodic reaction: $Cd - 2\,e \rightarrow Cd^{2+}$

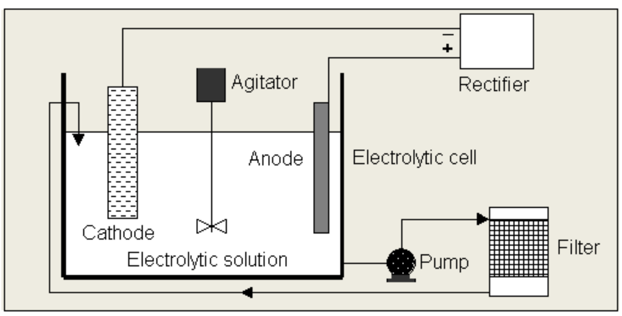

Fig 1: Electrolytic cell for deposition of cadmium

Electrolytic cadmium plating can be performed in acid as well as alkaline cyanide baths. The acid baths are based on cadmium fluoroborate, fluoroboric acid and boric acid with a pH of 3.0-3.5. Alkaline baths consist of mixtures of cadmium cyanide, sodium cyanide and sodium hydroxide with a pH greater than 8.5. The current density applied is on the order of 2- 6 A/dm^2 and voltage may range from 6-12 volts. The thickness and properties of a cadmium coating deposited depend on current density, salt concentration, bath temperature, pH, kind of the base metal (cathode), brightness enhancers used, and so forth. In choosing the thickness is fundamental to know the use and corrosive medium that this part or appliance shall be submitted. The thickness of cadmium coating for saline conditions must be not less than 25 μm.

After deposition the cadmium coating should be passivated to enhance anticorrosive protection or to from bright layers with other purposes. The passivation processes used are chromatization with chromic acid, acidic hydrogen peroxide (H_2O_2) and dilute nitric acid (HNO_3). Of those three techniques the more extensively used chromatization. The thickness varies from 0.1 μm to 2 μm. Moreover, the corrosion byproducts and vapors are toxic. However, and for this reason, cadmium electroplating is not used for protecting against corrosion metallic materials in contact with foods and pharmaceutics products.

3. ANALYSIS AND INSPECTION

Before an piece can de satisfactorily plated it fundamental that the surface shall be thoroughly cleaned, freed from oxide layer, fats, oils, greases and in a appropriate state to receive the coating. In order to assure good performance of cadmium coating in the finished product it is necessary to inspect it concerning the quality of deposition during the electrolytic process [9]. Usually the manufacturer carries out the deposition control process.

The buyer is allowed participate in order to ascertain the quality of the product. Their participation comprises: deposition technology evaluation, bath control techniques, equipment used to evaluate the deposit and surface treatment of the pieces to be coated. In operating plating solutions it is essential to make certain that the composition of the principal's chemicals remains approximately as the standard composition or original formula. Most plating solutions generally require small additions of the chemical products on long time of operation. The final quality evaluation of the coating should contemplate the following items: thickness, uniformity, adherence, porosity, holes, hydrogen embrittlement and corrosion resistance.

- **Coating Thickness and Uniformity**

The thickness of cadmium coating depends on their intended utilization. In Brazil the minimum thickness criteria for cadmium coatings on steel presented in are based on ASTM standard B 766-86 [10]. Minimum thickness criteria for cadmium coating on steel show: severe (12-25 μm), moderate (8μm) and mild conditions (5 μm). Usually the electrolytic processes furnish uniform deposits, however depending on salts concentrations, on additives used in the bath and on the operational conditions used during the cadmium coating. These defects are serious mostly when the coated piece is due to be exposed to aggressive conditions. The thickness of electrodeposited cadmium coatings shall be determined by methods B 487 [11], B 499 [12], B 504 [13], B 567 [14], as applicable. The figure 2 presents a metallographic of a cadmium-coated bolt.

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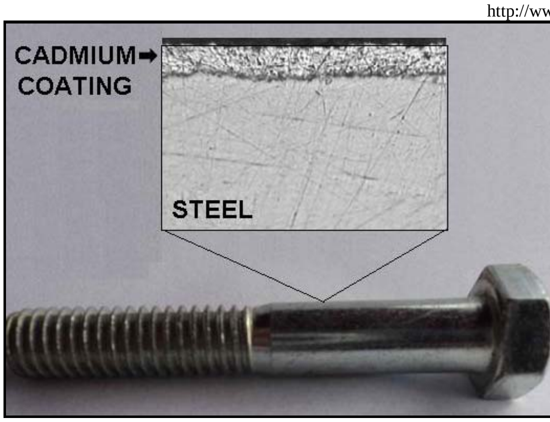

Fig 2: Metallographic of a cadmium-coated bolt

- **Adherence**

Usually cadmium coating show good adherence to the base metal. Adherence tests are qualitative and comparative and depending on the geometric characteristics of the piece are used specimens cylindrical or rectangular coated at the same time as the piece. They probably acquire the same coating characteristics of the piece itself. The most used test are of the bending or impact types as described on standard ASTM B 571 [15]. The figure 3 shows the aspects of a good and bad adhesion of a cadmium coating.

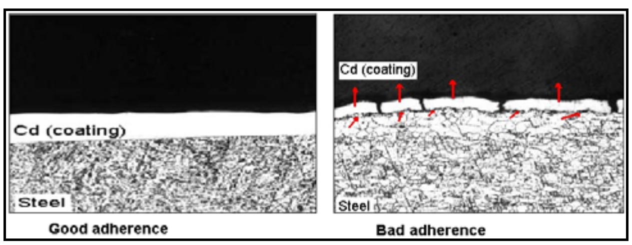

Fig 3: Metallography of a cadmium bolt with good and bad adhesion

- **Porosity and Cracking**

The cadmium coating should be free of porosities and /or cracks since this kind of defect allows the contact between the corrosive environment and the base metal. The thickness and the uniformity of the coating determine the porosity [16]. When the coating thickness is less than 5 μm a high porosity should be expected, but when it is greater than 10 μm no porosities are found.

- **Corrosion Resistance**

Cadmium coating shows good performance in marine atmospheres, although that performance is related to the thickness. According to Souza Jr. & Freitas [17] the thickness recommended for bolts in marine environments is at least 12 μm, nevertheless, when under spray or in complete immersion that thickness should be increased. However the cost to get bolts with 25μm is very high and not always that increase in the cost on the thickness compensates the increase in the anticorrosive protection obtained. Money and Kain [18] show that cadmium coating is superior to the zinc coating in various environments except in seawater.

Kajimoto, Almeida and Siqueira [19], who have made atmospheric corrosion researches at São Paulo state, observed a low corrosion resistance of cadmium coatings in industrial atmospheres rich in sulfur dioxide (SO_2) and suggested that periodical inspections should be made in cadmium coated equipments because of the need to substitute them caused by the low thickness of the coatings.

- **Hydrogen Embrittlement**

Carbon steel hydrogen embrittlement, principally of steels of high resistance, may happen in acid stripping or during electrolytic deposition of cadmium. This kind of attack occurs during the acid removal of corrosion products adhered to the carbon steel surface, when steel is attacked by acids (hydrochloric acid) shown below:

$2\ HCl + Fe$ (carbon steel) $\rightarrow FeCl_2 + 2\ H$ (atomic hydrogen)
$2\ H \rightarrow H_2$

This problem may be overcome or minimized with suitable corrosion inhibitors which allow adherent oxides removal and avoid or inhibit atomic hydrogen evolution and in that way decrease the probability of hydrogen embrittlement.

Hydrogen embrittlement on cadmium coatings is greater in acid plating baths than in cyanide based alkaline ones due to the cathodic reaction as a function of pH acid (**$2H^+ + 2e \rightarrow 2H$**). High values of atomic hydrogen (H) increase hydrogen embrittlement susceptibility [20].

Heating during 2 hours at 180°C is recommended for hydrogen removal on cadmium coatings. The susceptibility to hydrogen embrittlement may be evaluated according to the ASTM standard F 519-06 [21] and F 1940-01 [22].

- **High Temperature Evaluation Test**

The melting and boiling points of cadmium are, respectively, 320.9° C and 735°C. Because of its low boiling point and high vapor pressure cadmium if easily during the merger and condenses in the form of particles fine which react immediately with oxygen, turning into cadmium oxide, inhalable form and extremely toxic [23]. The purpose of this test is to evaluate the possibility of contamination by vaporization when cadmium coatings are working at temperatures in the range 120-220°C, according to the figure 4.

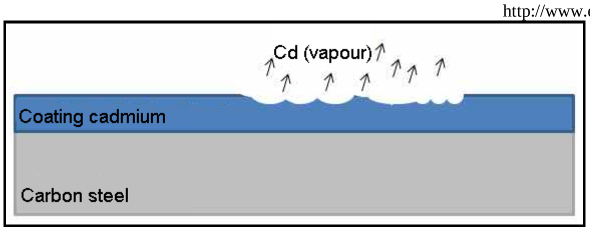

Fig 4: Illustration of the vaporization of cadmium coating

The laboratory test methodology is to encapsulate the bolts coating cadmium (specimens) in special glass bottle (10 mL) with aluminum cover and polymeric silicone septum as shown in figure 5.

Fig 5: Special glass bottle (10 mL) with aluminum cover and polymeric silicone septum

Then the specimens are placed in the oven, at room temperature of 120 to 220° C by 4 hours. After the cooling of specimens was conducted analysis of coating cadmium vaporized retained in the glass bottle. The vaporized cadmium was determined by differential pulse voltammetry [24] whose results are presented in the graph in figure 6. The chemicals analysis shows that the increase of temperature causes coating vaporization, allowing dangerous contaminations.

This fact means that the use of cadmium coating may cause contamination of food and pharmaceuticals.

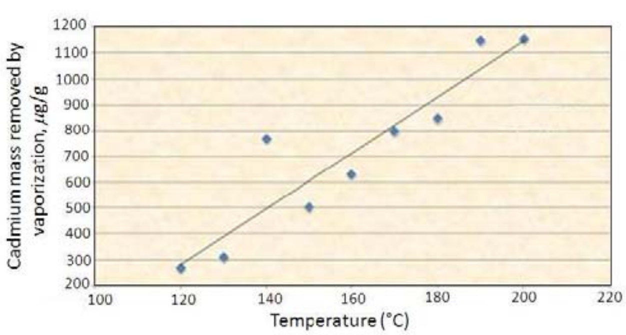

Fig 6: Cadmium mass removed by vaporization as a function of temperature

4. CONCLUSIONS

Based on the cited references and on laboratory tests we may conclude that:

- To ensure cadmium coatings performance, the deposition process must be known and procedures of inspection during processing and for the end product have to be fixed;
- At the final inspection of cadmium coating the followings test should be made: uniformity, porosity, adherence, corrosion resistance and susceptibility to hydrogen embrittlement;
- Cadmium coatings must not be used at temperatures above 120°C, because cadmium vaporization may cause contaminations;
- Cadmium coatings made from cyanide plating solutions are less prone to hydrogen embrittlement than those made from acid plating solutions;
- Electrolytic cadmium plating carried in cyanide solutions is very toxic, therefore, can be used since that effluent treatments are carried through;
- Cadmium coatings couldn't be used in equipments of food, pharmaceutical and correlated industries;
- It is very important that the society has knowledge of the toxic effect of the cadmium in the environment.

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