

CORROSION FAILURE OF ELECTROPLATED COATINGS

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Abstract

Corrosion failure of metallic electroplated coatings on various products were analysed and the dominant corrosion stimulators were identified. The thickness and porosity of coatings are very important for their corrosion resistance. The suitable thickness of these coatings shall be chosen from the technical standards recommendations depending on the severity of service conditions. This characterisation of corrosion risks are not fully respect in other products standards, e.g. for electronic products, devices and installations. In articles the examples of how different of environment fit into the corrosivity classification system are given.

Keywords: electroplated coatings, corrosion properties, corrosivity of environments, technical standards

1. INTRODUCTION

Electroplating is a widely used technique because it can plate a variety of metals onto a variety of substrates to produce smooth coatings. Electroplating has wide usage in many industries for creation decorative and/or technical coating which also provides corrosion protection. The corrosion protection durability of these coating depends on few factors:

- type of metallic coating – the corrosion resistance of this metal,
- type of substrate metal – anodic or cathodic metallic coatings protect substrate by the different mechanisms,
- properties of coating – thickness, porosity, homogeneity, etc.,
- corrosivity of the exposure/service conditions.

The technical requirements of metallic coatings are specified in standard ISO EN 27830 *Metallic and other inorganic coatings — Standard guide for specifying metallic and other inorganic coatings*. The service condition number designates the severity of the conditions that the coating will be subjected to in service - Annex C (Table 1).

Table 1 Examples of service conditions

Service condition	Description of the severity of service conditions
1	<i>Mild</i> - Exposure indoors in normally warm, dry atmospheres with minimum wear and abrasion
2	<i>Moderate</i> – Exposure indoors in places where condensation of moisture may occur, as in kitchens and bathrooms
3	<i>Severe</i> – Service outdoors where occasional or frequent exposure to rain, dew, strong cleaners and saline solutions may occur
4	<i>Very severe</i> – Service outdoors that is likely to include denting, scratching and abrasive wear in addition to exposure to corrosive environments; e.g., as in marine and industrial applications
5	<i>Extended very severe</i> - Service outdoors that is likely to include denting, scratching and abrasive wear in addition to exposure to corrosive environments where <i>long-time</i> protection of the substrate is required; e.g., conditions encountered by some exterior components of automobiles

Service conditions are taken into consideration when selecting the coating designation. The relation between service condition number and the designation including thickness recommendations may be found in many of standards covering specific coatings.

2. CORROSION BEHAVIOUR OF ELECTROPLATED COATINGS

The electroplated metallic coatings are deposited from metals as zinc, zinc alloy, nickel, copper, tin, cadmium, silver, etc. For some metallic coatings their corrosion rate shall be considered as the same as metal matrix (zinc, copper, silver according to EN ISO 9223 and/or ISO 11844), for the other the corrosion rate is estimated from filed atmospheric tests – Table 2. These values are the first year corrosion rates.

Table 2 Atmospheric corrosion rate of metallic coatings

Metallic coating	average corrosion rate ($\mu\text{m}\cdot\text{a}^{-1}$) at corrosivity category				
	C1	C2	C3	C4	C5
zinc	0.10	0.40	1.40	3.15	6.30
copper	0.10	0.35	0.95	2.05	4.20
silver	0.15	0.95	-	3.42	-
nickel	-	0.25	0.60	-	2.80
tin	-	0.50	0.70	-	2.00
cadmium	-	-	4.10	6.90	11.80

The protective effect of metallic coatings is given by their polarity to substrate metal (see Fig. 1):

- Anodic coatings for the protection of iron and steel substrates are almost entirely limited to zinc and aluminium coatings or their alloys. The mechanisms of corrosion protection inferred by these coatings are obtained by cathodic protection and a barrier to the environment. The efficiency of protection is given by thickness of coating and corrosivity of exposure environment.
- Cathodic coatings are those which comprise a coating metal which is cathodic with respect to the substrate (Ni, Cr, Cu, etc.). Cathodic coatings can provide excellent corrosion protection. If the substrate is exposed to the corrosive environment, the substrate will become the anode and corrosion will be dramatically accelerated resulting in spalling of the coating. Thick coatings will provide better protection than thin coatings.

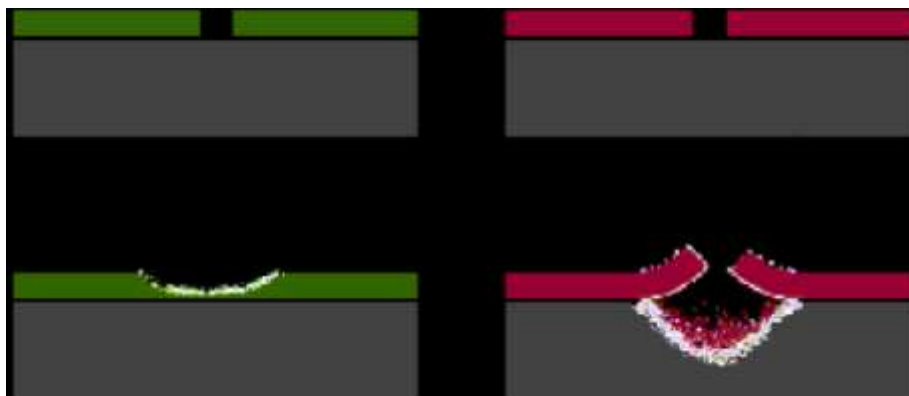


Fig. 1 Protective mechanisms of anodic and cathodic coatings

3. CASES STUDIES OF ELECTROPLATED METALLIC COATINGS

3.1. The effect of coating thickness

The part of assembly of locomotive engine is produced from aluminium alloy and for the high reflectance properties is covered by silver coating. The thickness of silver coating was ca 3 μm . After 3 months of service at urban/marine environment the failure of coating was reported – Fig. 2.



Fig. 2 Failure of silver coating on aluminium

The failure was not caused due to corrosion of silver coating but as the very thin coating was very porous the substrate aluminium corroded by the typical pitting mechanisms and the silver coating lost adhesion to substrate. This failure mechanisms was proved by accelerated corrosion test in neutral salt spray NSS according to EN ISO 9227 *Corrosion tests in artificial atmospheres — Salt spray tests*. It was recommended to apply multilayer coating to increase the corrosion protection – nickel + silver. The results of accelerated test on Fig. 3 show the effect of coating thickness. The recommended thickness for electrodeposited coating which shall give the long-term corrosion protecting in open atmospheric conditions is minimum 25 μm – this thickness is sufficient to eliminate the porosity of coatings.

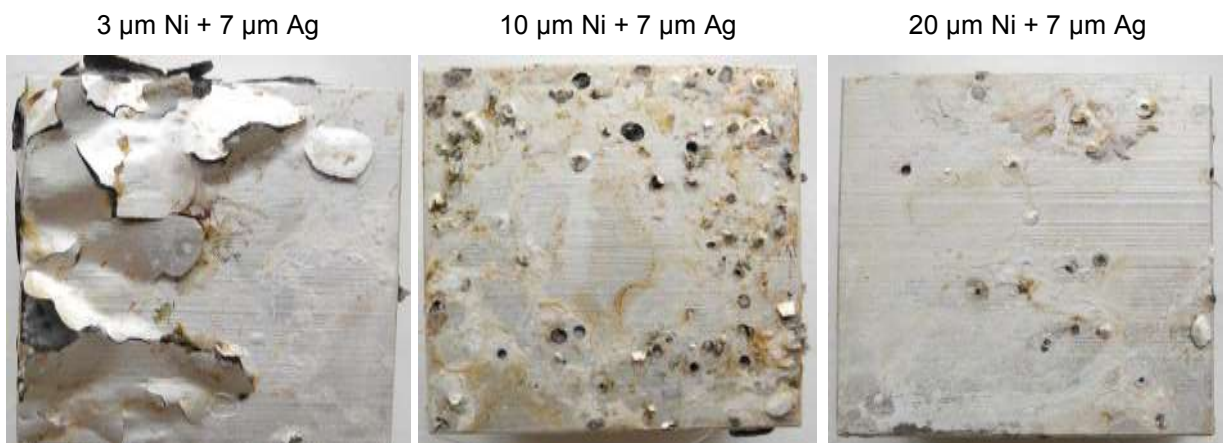


Fig. 3 Corrosion resistance of nickel/silver coatings with various thicknesses on aluminium

3.2. Corrosion of metallic coating during transport

Atmospheric contaminants promoting the corrosion are dissolved in the thin layer of electrolyte over metals as a consequence of even low relative humidity (RH) and create relative thin layer of corrosion products. These corrosion films can form an insulating layer on the contact surfaces causing electrical failures on the electric and electronic devices. In case of electric and electronic elements shown on Fig. 4 the total failure due to corrosion was caused by non-suitable protection during transport from the Czech Republic to East Asia country. The overseas shipping transport took ca 8 weeks.

Generally corrosion in micro or power electronics depends on several variants such as the package type, materials involved, assembly processes, moisture, inorganic and organic contaminants, atmospheric pollutants, temperature, thermal stress and electrical bias. Metallic products can only be protected by suitable packaging against atmospheric influences if all expected atmospheric conditions during storage, interim storage, handling and transport have been known and carefully assessed when designing the packaging. This includes knowledge of temperatures, air humidity levels, precipitation etc.

IEC 60721-1 *Classification of environmental conditions – Part 1: Environmental parameters and their severities* is series of standards specifying service condition for electric devices including storage and transport. The corrosion stress can be derived from the combination of climatic and pollution parameters (salt fog, SO₂, H₂S, etc.) and expressed as class, e.g. 3C2. Not respecting the basic principles of corrosion protection caused such total damage – the main factors were high humidity and water condensation in packaging box.



Fig. 4 Electric and electronic elements' corrosion caused by non-suitable protection during transport

3.3. Corrosion of electric elements in specific indoor conditions

In many cases the service conditions are not specified according to this “corrosion/coating” standard but according very different standards specified the product properties and/or their durability in various service conditions respectively corrosive environments. The example shall be electro technical and electronic products which have many parts covered by electroplating coatings and are used in very different conditions/environments. These conditions are specified according standards for electric products, e.g. Czech standard CSN 33 2000-3 *Low-voltage electrical installations - Part 1: Fundamental principles, assessment of general characteristics, definitions*, which is the Czech version of the Harmonization Document HD 60364-1, and the main focus is given to protection against electric shocks, thermal effects, overcurrent, voltage disturbances and electromagnetic disturbances. The risk of corrosion and subsequently follows failure of function is not evaluated. For estimation the corrosion risk the one from IEC 60721-1 series should be used or similar standards for estimation the degree of pollution as IEC 61010 *Safety requirements for electrical equipment for measurement, control, and laboratory use*. Requirements for the qualification of coatings for protection against pollution are in Annex H of IEC 61010.

The LED diode lighting was installed over the swimming pool (Figure 5). The socket is made from plastic material covered by metallic coating of copper, nickel and chromium. The indoor environment was specified as AF1 corrosion risk is negligible even the thermal water containing H_2S is used in pool and chlorine as densification is applied regularly, too. The corrosion damage was so intensive that after 1.5 years of service the lighting collapsed.



Fig. 5 LED diode lighting of swimming pool and the their corrosion after 1.5 years of service

The conditions over the pool were measured – Table 3 – and the corrosion risk was estimated as AF4 according to CSN 33 2000-3. LED diode lighting was installed over the swimming pool (Figure 6). The effect of H_2S was not included even the water contains 5 – 12.8 mg.L⁻¹. The socket is made from plastic material covered by metallic coating of copper, nickel and chromium. The indoor environment should be specified as service condition number 4 or 5 according to ISO EN 27830 which means the electrodeposited coating thickness has to be much higher than was used – Table 4. The coating composition and thickness are specified according to ISO 4525 *Metallic coatings - Electroplated coatings of nickel plus chromium on plastics materials*. The influence of air pollution by hydrogen sulphide and chloride onto corrosion attack of metallic coating was proved by elementary analysis and x-ray diffraction analysis – Table 5 (Fig. 5). The identified dominant compound was atacamite $Cu_2Cl(OH)_3$ and nickelboussingaultite $(NH_4)_2Ni(SO_4)_2(H_2O)_6$. These results also reflect the sensitivity of each metal to air pollution.

Table 4 Coating thickness for various service condition numbers according to ISO 4525

coating	Service condition number
PL/Cu 15a/Ni10d Cr mp (mc) PL/Cu 15a/Ni15b Cr r	2
PL/Cu 15a/Ni25d Cr mp (mc) PL/Cu 15a/Ni30d Cr r	4

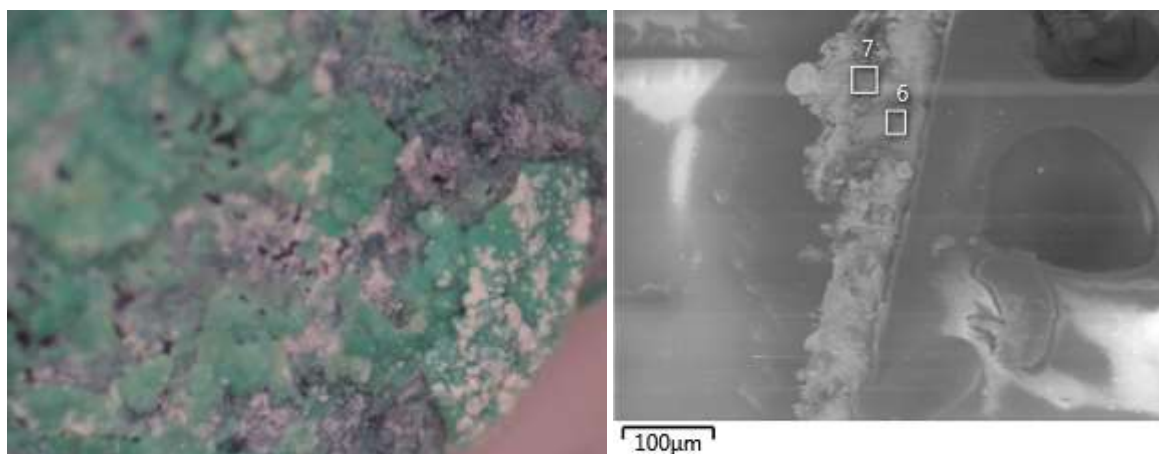

Fig. 6 Corrosion products layer on diode socket (light microscope and cross-section BES image from electron scanning microscope)

Table 3 Conditions over the pool

parameters		classification of conditions	
		CSN 33 2000-3	IEC 60721-1
air temperature (°C)	29.8	AA5	3K3
relative humidity (%)	52.0	AB6	3K6
water	yes	AD4	3Z9
Cl ⁻ concentration (mg.m ⁻³)	1.85	-	3C2
Cl ₂ concentration (mg.m ⁻³)	1.24	AF4	3C1

Table 5 Elementary composition of corrosion products (wt. %) (Fig. 5)

Al	Si	S	Cl	Ca	Cr	Ni	Cu	Zn	Br	Sn
0,08	0,60	15,91	12,95	0,32	0,36	4,67	62,56	0,27	1,93	0,36

CONCLUSION

Early failure of products, parts with electrodeposited metallic coating may be mainly caused by:

- defective design;
- defective manufacturing;

- defective material; and
- non-suitable coatings/substrate materials for environment.

There are many reasons of premature failing of electrodeposited metallic coatings but the non-suitable their specification in respect to expected service conditions is one of the most frequent. The understanding of protective function of each type of these coatings and substrate matrix is necessary.

The very different system for specification/classification of environmental conditions for the coatings themselves and final products on the other hand created in different standardization bodies increase the mess and lead to significant economic loss.

ACKNOWLEDGEMENTS

The study was elaborated in frame of the project IP 3/2015 financed by Ministry of Industry and Trade of the Czech Republic.