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CHROMATE-FREE PRETREATMENT FOR METALLIC SURFACE

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Legislațiile recente impun limitări drastice în ceea ce priveşte folosirea în viitor a cromului hexavalent în industrie, datorită considerentelor de sănătate şi mediu. In consecință, este necesar să se dezvolte o alternativă la pre-tratamentele pe bază de crom folosite pentru creşterea rezistenței la coroziune şi a durabilității acoperirilor pentru suprafețe metalice.

Prezentul articol studiază rolul unei soluții pe bază de butiltitanat folosită ca pre-tratament al suprafețelor de oțel galvanizat şi aluminiu în vederea realizării unei protecții anticorozive fără crom.

Recent legislation imposes a strong limitation in future of hexavalent chromium use in industry due to health and environmental considerations. There is consequently a need to develop alternative pre-treatment processes in order to improve corrosion resistance and durability of galvanized steel and aluminum coatings

The purpose of the present work is to study the role of a butyl titanate based solution in surface pre-treatment of galvanized steel and aluminum as a premise for development of chromate-free anticorrosion protection.

Keywords: corrosion protection, chromate-free pretreatment, butyl titanate, aluminum coatings

1. Introduction

Chromate treatment has been widely used as an anti-finger electro-galvanized steel sheet to ensure corrosion resistance. In spite of excellent corrosion resistance [1,2] the uses of chromate based corrosion inhibitors are undesirable for safety control in industrial uses and protection of the environment. The soluble hexavalent chromium remains on the surface and has toxicity to human beings and environment. Surface treatments with chromium compounds must be prevented from industrial uses in the near future. Therefore, the number of researches dealing with the exploration and development of effective substitutes for chromates has considerably increased in the last years. Among them the sol-gel or ceramic like thin films takes a significant part [3-5]. For

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example, it has been reported that the covering of the surface of stainless steel with TiO_2 nanoparticles by using a dip-coating technique leads to sufficient improvement of corrosion resistance properties. However, the protection mechanism of such a coating implies that they can work only until their surface is intact. As soon as even small defects appear in the sol – gel of TiO_2 layer, these coatings are no longer able to protect the exposed zone.

The development of new coating systems with active corrosion protection instead of the carcinogenic chromates is an issue of prime importance for the wide range of industrial applications where effective corrosion protection is required. Active protection implies not only mechanical covering of the protected surface with a dense barrier coating but also provides self-healing properties which allow continued protection even after partial damage of the coating.

Usually the coating system consists of several layers including a pre-treatment layer applied directly to the metal surface and one or several organic coating layers. Although the main function of pre-treatment is to provide a good adhesion of paint to the metal, enhancement of its protective properties is very desirable as well.

Titanium alkoxides are economical and environmentally friendly and may be used to protect the surface of various metals. Formation of a stable and uniform coating film for corrosion protection has been actively investigated. Butyl titanate film has been deposited on the metallic surfaces by immersion from alcoholic solution followed by heat treatment at 110°C. The process is energy-intensive due to the post-heat treatment at 110°C for 20 minute, and is not commercially viable. In the absence of a heat-treatment, butyl titanate adheres on the substrate and dissolves rapidly in aqueous media [6, 7]

In the present paper, we explore and develop a novel solution using butyl titanate as pre-treatment of metallic surfaces to improve their corrosion resistance. Uniform and adherent butyl titanate layers have been deposited by a single step immersion of metallic panels (galvanized steel or aluminum panels) in a bath of butyl titanate in n-buthanol-isobuthanol (1/1) solution, followed by the drying at room temperature [8].

2. Experimental

The immersion bath used was a 5% butyl titanate in n-buthanol-isobuthanol (1/1) solution. The metallic samples used were galvanized steel or aluminum panels with 116 cm^2 surface area. Surface morphology of the coatings was analyzed by SEM with CPII Scanning Probe Instruments, Veeco Instruments. Constitutive elements on the surface of the panels were analyzed using energy dispersive analysis with X-rays (EDAX).

The corrosion resistances of all panels were evaluated in 5% NaCl solution at pH 5.0. Accelerated corrosion testing was carried out using a dry corrosion test cabinet from Angelantoni Industries SpA model DCTC_F00231. The samples were exposed to a constant 5% salt fog in accordance with ISO 7253 specification. The appearance of the white rust, red rust and failure of the samples were observed as a function of time. The basis for the failure criterion was determined as 5% red rust on the surface of the samples.

3. Results and discussion

1. Preparation of anticorrosive protection film of butyl titanate

Initially, the metallic panels of galvanized steel or of aluminum were degreased with acetone or toluene (to move out the impurities like metallic oxides, oils) and washed with demineralized water. Then, the panels were immersed in 5% n-buthanol-isobuthanol (1/1) solution of butyl titanate bath. The immersion (the deposition) was performed at room temperature for 15 minutes. Subsequent to deposition, the samples were dried in air at room temperature for 2 h. Visual observation showed a smooth and transparent titanium alkoxide film.

The microstructure and the thickness of the titanium alcoxide coating were analyzed by cross-sectional studies at high magnification under scanning electron microscopy (SEM).

Fig. 1 is a SEM image of aluminum surface. The titanium alkoxide coating reproduces the substrate morphology of underlying aluminum substrate, indicating the uniformity of the thin layer of titanium alkoxide deposit.

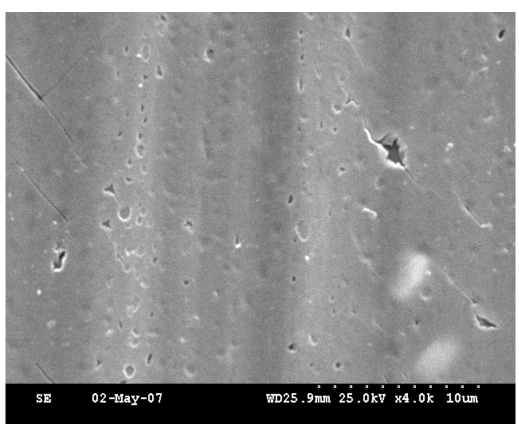

Fig. 1.Cross-sectional SEM image of the aluminum panel coated with butyl titanate

Fig. 2 shows the EDAX spectrum of the above mentioned sample. The EDAX method was used to obtain a relative estimation of the deposited butyl titanate (the presence of titanium).

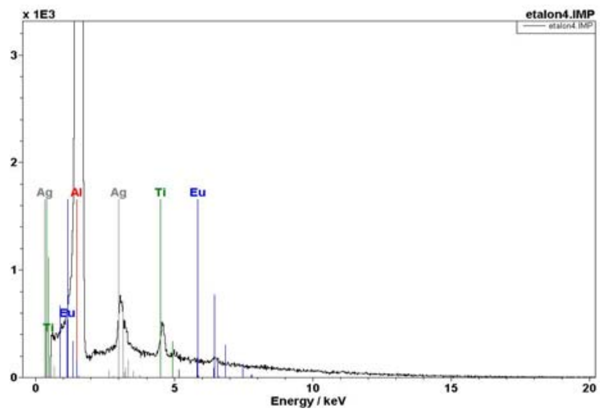

Fig. 2. EDAX spectrum of aluminum treated with butyl titanate

A homogenous and dense titanium alkoxide layer tightly anchored to aluminum substrate, probably with –O-Ti-O-Al – bonds, is observed. The thickness of the titanium alkoxide layer deposited is approximately 500 – 600 nm. Also, the cross section reveals the presence of two distinct layers, a thin layer immediately over metallic aluminum, followed by another thick layer [8].

*2. Study of **c**orrosion performance in comparation with other commercial coatings*

Since the objective of the present work is to substitute the toxic chromate coatings with environmentally friendly coatings, it is imperative to analyze the corrosion proprieties of butyl titanate coatings and to compare them with the commercial passivity processes.

Salt spray testing was performed in order to evaluate the coating performance under accelerated corroding condition. Table 1 summarized the results obtained from the salt spray chamber study performed in compliance with ISO 7253 standards.

Table 1

Results of ISO 7253 accelerated corrosion testing for various coatings

Time of exposure (hour)	White rust	Red rust	Failure
Galvanized steel	24	48	48
Galvanized steel/phosphate	48	144	192
Galvanized steel/butyl titanate	60	155	220

The failure criterion was 5% surface coverage with red rust. Galvanized steel sample without any passivity or coating failed in a span 48 h. Among the commercially available coatings, the passivity with phosphate pretreatment is the highest. In the presence of a thin butyl titanate layer, salt spray corrosion time extends to nearly 10 times over the untreated galvanized steel. A comparison of the corrosion data of the panels shows the improved performance of the titanium alkoxide coatings.

4. Conclusion

A novel chromate-free pre-treatment based on butyl titanate has been developed. SEM studies relived the presence of a homogenous and dense titanium alkoxide layer tightly anchored to aluminum substrate. This coating process can also apply to other metallic substrates like iron or zinc.

A comparison of the corrosion data of the metallic panels covered with butyl titanate thin film as pre-treatment of the metallic surfaces with that of commercially coatings shows the improved performance of the titanium alkoxide coatings.

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