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Resistance of Chromated Zinc Coatings to the Impact of Microscopic Fungi

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Zinc coatings are used to protect metallic parts of automobiles from corrosion. Zinc protective coatings are often chromated additionally treating them in acidic solution of chromium compounds. In recent years new technologies were designed to deposit chromate films of various thickness and resistance on zinc surface from acidic solution of Cr(III) compounds. It has been noticed, that under atmospheric corrosion conditions microscopic fungi are present in the environment affect zinc coating. The aim of the presented study was to determine if zinc coatings treated with Cr(III) solution become more resistant to fungi influence or their resistance diminishes. The analysis of steel plates coated with a zinc film and treated in four different chromium solutions has shown that in all the specimens fungi of *Cladosporium herbarium* species were detected and their frequency of detection was quite high, sometimes up to 50 %. However, we failed to determine the regularities of distribution of some fungi on the surface of plates chromated in different solution. The comparison of changes in the surfaces of plates treated with the four solutions has shown that the plates treated in the Likonda 3Cr5 passivation solution changed least after being exposed to atmospheric conditions. Chromated plates contaminated with mixtures of different fungi and kept for 60 days at a temperature of (26 ±2) °C under humid conditions were examined by using a scanning electron microscope (EVO 5O XP Carl Zeiss STM AG, Germany) and the peculiarities of their surface damage were determined. The peculiarities of growth of some fungi species were determined on the plates chromated in the Likonda 3Cr5 and $Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid solutions. Under these conditions the fungi of *Chrysosporium merdarium, Fusarium proliferatum, Paecilomyces lilacinus, Penicillium stoloniferum* can either generate and promote the damage of metal surface or stabilize its corrosion processes.

Keywords: steel corrosion, zinc coatings, chromium solution, microscopic fungi.

1. INTRODUCTION

Metal corrosion and its inhibition have been studied extensively worldwide. In recent years acidic metal passivation solutions containing Cr(III) are being used more and more often to protect metals from corrosion as they are less hazardous to the environment as compared to those containing Cr(VI), which are considered to be extremely toxic. However some authors [1, 2] state, that iron corrosion and its inhibition in acidic Cr(III) passivation solution possesses some specific features. Here corrosion proceeds in the mixture of several components of passivation solution, in the certain pH interval, simultaneously with zinc dissolution and formation of conversion film. In this case corrosion inhibitors have to impede iron dissolution during passivation and protect the surface of steel not covered with the zinc coating from accumulation if metabolites which are formed owing to the antropogenic – biologic influence during their treatment and storage. It is very important, that inhibitors should not impede zinc passivation and should not diminish the protective and decorative properties of conversion coatings.

The process of metal corrosion and inhibition, and thereby the courses of passivation, can be governed by microscopic fungi spread in the environment. Fungi can solubilize minerals and metal compounds through several mechanizms, including acidolysis, complexolysis, redoxolyzes and by metal accumulation in the biomass. Organic acid excretion by fungi is inter- and interaspecific and can be strongly influenced by the presence of toxic metal [3, 4]. Fungal derived carboxylic acids with strong chelating properties (oxalic acid, citric acid) can aggressively attack mineral surfaces [5, 6].

The quality of corrosion protection afforded by a particular type of zinc conversion coating is often thought to be a mere function of the Cr(VI) content. The corrosion protection also increases with a higher film thickness. A comparison of conventional chromate conversion processes employing Cr(VI) and alternative processes based on Cr(III) has shown that conventional yellow chromate (e. g "Corro Yellow") passivation provides more corrosion protection than blue passivation. It has both a higher thickness (approximately 0.3 μm) and a higher chromium content (in the region of 70 $mg \cdot m^{-2}$ to 90 $mg \cdot m^{-2}$) [7].

A conventional chromate coating has a superior corrosion resistance but its usage has been limited by several environmental legislations – as it displays high toxicity for human health and causes serious environmental pollution, while trivalent chromium has low toxicity and the waste water and solid waste from the Cr(III) bath can be treated in a simple and efficient way. The Cr(III) conversion coating treatment is one of the potential alternatives to the chromate conversional coating (CCC) process for zinc – coated steels [8]. The corrosion rate of metal protected by an organic coating is related to: the transport of ions across the coatings, charge transfer processes at the metal-coating interface, delamination and changes in the composition of organic matrix. The corrosion behavior was studied by polarization curves and electrochemical impedance spectroscopy in the 3.5 % NaCl solution at room temperature. Morphological

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characterization of the coating surface was also performed. The results indicate that the Cr(III) passivated coating with sealing treatment has a high corrosion resistance and it could be a less polluting alternative to the traditional Cr(VI) passivated coatings [9].

Microbially influenced corrosion (MIC) refers to processes of metals caused by microorganisms adhering to the interfaces usually called “biofilms”. It is well known influence of microorganisms on the kinetics of corrosion that the metabolitic activity of clusters of biofilm organisms can change pH for more than three units locally. In that way MIC is caused by the effect of microoganism on the corrosion kinetics and showed that microorganisms are involved into the process [10 – 12].

The main purpose of the present work was to find a substitution for toxic Cr(VI) in chromate solution and to diminish both the corrosive potential of steel and the environmental hazard by keeping or even increasing the effectiveness of zinc coatings chromated in the trivalent chromium solution with the help of electrotechnical and microbiological measures.

2. EXPERIMENTAL METHODS

Solution of Cr(VI), $Cr(NO_3)_3 \cdot 9H_2O$ and its complex with organic acid as well as several commercial solutions containing the Cr(III) complex with an organic acid and additionally Co^{2+}, F^-, SO_4^{2-} ions were used for investigations. The concentration of chromium was (4 – 5) $g \cdot l^{-1}$, pH = 2.0, the duration of passivation was 60 seconds, the temperature was (15 – 18) °C. The methods of preparation of solutions and steel surface were discribed by V. Rėzaitė et. al., 2009 [13].

Specimens with an area of 50 cm^2 and a thickness of 0.7 mm made of cold rolling carbon steel of grade 0.8 ps (Russia GOST 9045-93) containing C – 0.05, Si – 0.02, Mn – 0.29, S – 0.018, P – 0.012 %.

Atmospheric corrosion studies were carried out in the suburb of Vilnius, Visoriai, according to standard ISO 9226 1992 (Corrosion of metals and alloys – corrosivity of atmosphere. Determination of corrosion rate of specimens for evaluation of corrosivity).

Micromycetes were isolated from the metal specimens in atmospheric corrosion test sites in two way: a) by direct isolation from the surface of plates using a sterile metal loop; b) by preparing suspensions from rinsing water of plate surface of known area in sterile water (1 : 10; 1 : 100; 1 : 1000; 1 : 10000) and later the determined quantity of micromycetes sowing on the agar media of known composition: malt agar and Sabouraude's medium enriched with 0.5 $g \cdot l^{-1}$ of chloramphenicol were used. Samples were incubated for 5 – 7 days in a thermostat at (26 ±2) °C. The results were expressed as colony forming units (CFU) per 1 cm^2 area of a specimen. Abundance of mycrobiots was determined by applying the quantitative methods [14].

The colonies of microscopic fungi were subcultured in order to obtain monocultures. Their cultural properties were discribed, indicating the growth rate, colony structure and appearance, colour of mycelium and reverse of the colony and other properties.

A microscope BI 500 (VWR) and scanning electron microscope EVO 50 EP (Carl Zeis SMT AG, Germany) was used to characterize the morphologic peculiarities of each fungal species and the process of conidiogenesis as well as to characterize the morphology of the steel surface. The systematic position was determined according to various manuals.

The Siorensen (Sőrensen) coefficient K_S was calculated and used to compare the micromycetes complexes grown on plates passivated in different solutions:

$$K_S = \frac{2N_{A+B}}{N_A + N_B} \cdot 100\%, \qquad (1)$$

where N_{A+B} is the number of species common for both compared complexes; $N_A + N_B$ is the total number of species of the compared complexes A and B.

Two complexes of micromycetes under comparison really differ when K_S is less than 50 %.

The complexes of the fungi species compared were detected on the Zn coating chromated in the following solutions: 1. $Cr(NO_3)_3 \cdot 9H_2O$, 5 $g \cdot l^{-1}$; 2. $Cr(NO_3)_3 \cdot 9H_2O$, 5 $g \cdot l^{-1}$ + malonic acid; 3. Likonda 3Cr5; 4. Likonda 3CrV; 5. Likonda 3CrMC; 6. Likonda 3Cr5 + paste* (*solutions: 5 $g \cdot l^{-1}$ $Cu(NO_3)_2 \cdot 3H_2O$; 5 $g \cdot l^{-1}$ $FeCl_3 \cdot 6H_2O$; 100 $g \cdot l^{-1}$ NH_4Cl, paste 14 ml $Cu(NO_3)_2 \cdot 3H_2O$ + 66 ml $FeCl_3 \cdot 6H_2O$ + + 20 ml NH_4Cl + 60 g kaolin).

Rentgenograms were recorded with an X-ray diffractometer D 8 (Bruker AXS, Germany, 2003). Cu K_α radiation and a multilayer Ni/graphite monochromator were used. The method of sliding X-ray (the angle of X-ray to the specimen surface was 0.5°) was applied. The detector scanning step was 0.02°, the time of impulse accumulation was 8 s.

The mass loss of coating was determined by the following method: prior to exposure coatings (plates) were washed with deionized water, dried in the air, 24 hours kept in an exicator with P_2O_5 then they were weighed. The same procedure was repeated after exposure (after 0.5, 1, 1.5, and 2 years). After that the changes in mass were calculated.

To determine the coating mass loss due to corrosion, the products formed during the process were removed by using the methods and the procedure described in the ISO 8407:1991 (E) standard: a) exposing for 3 min to CH_3COONH_4 solution at a temperature of 70 °C; b) washing with deionized water; c) drying in an exicator with P_2O_5 for 24 hours; d) weighing.

The atmospheric tests of metals and coatings were carried out according to the requirements of ISO 8565, 1992 (Metals and alloys. Atmospheric corrosion testing. General requirements for fields tests). The metal damage was evaluated by the methods described in ISO 10289, 1999 (Method for corrosion testing of metallic and other inorganic coatings on metallic substrates, Rating of test specimens and manufactured articles subjected to corrosion test).

3. EXPERIMENTAL RESULTS

3.1. Mycocontamination of the sample

Steel plates covered with Zn coatings and chromated in different solutions were contaminated with microscopic fungi to a variable degree after one year exposure to the natural environmental conditions (Vilnius, Visoriai) (Fig. 1).

Least fungi were collected from the plate whose Zn coating was passivated with the $Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid solution (Figs. 1 – 2). To compare micromycetes complexes, the composition of species the Siorensen (Sőrensen) coefficient was used. When its value is less than 50 % it can be stated that the complexes compared really differ according to the composition of fungi species.

The contamination of rain waters with propagules of microscopic fungi, after its flowing through the surface of the same plates coated with Zn coatings chromated in different solutions was higher than just studying a dry surface of the plates. And in this case the water flown through the steel plates coated with the zinc coating chromated in the $Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid solution (Fig. 2) was contaminated with fungi too.

The data presented in Table 1, a, show that the composition of the fungi detected on the steel plates coated with Zn coatings chromated in different solutions markedly differed, especially plate 2 chromated in the $Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid solution.

It has been noticed that in washing waters of some chromated plates there are abundant fungi of one species (Likonda 3CrV). According to the data in Table 1, b, the specific composition of fungi detected on zinc coatings passivated in different solutions really differed.

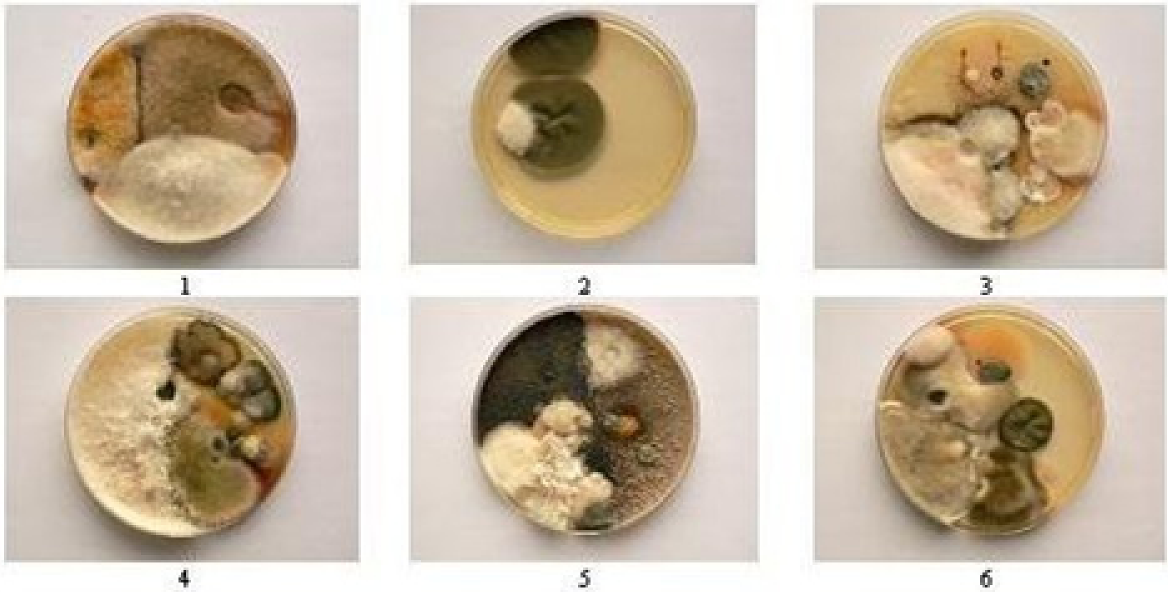


Fig. 1. Contamination with the propagules of fungi of steel plates coated with Zn chromated in different solutions after 1 year exposition to natural atmospheric conditions (Vilnius, Visoriai). Test solutions: 1. $Cr(NO_3)_3 \cdot 9H_2O$; 2. $Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid; 3. Likonda 3Cr5; 4. Likonda 3CrV; 5. Likonda 3CrMC; 6. Likonda 3Cr5 + paste

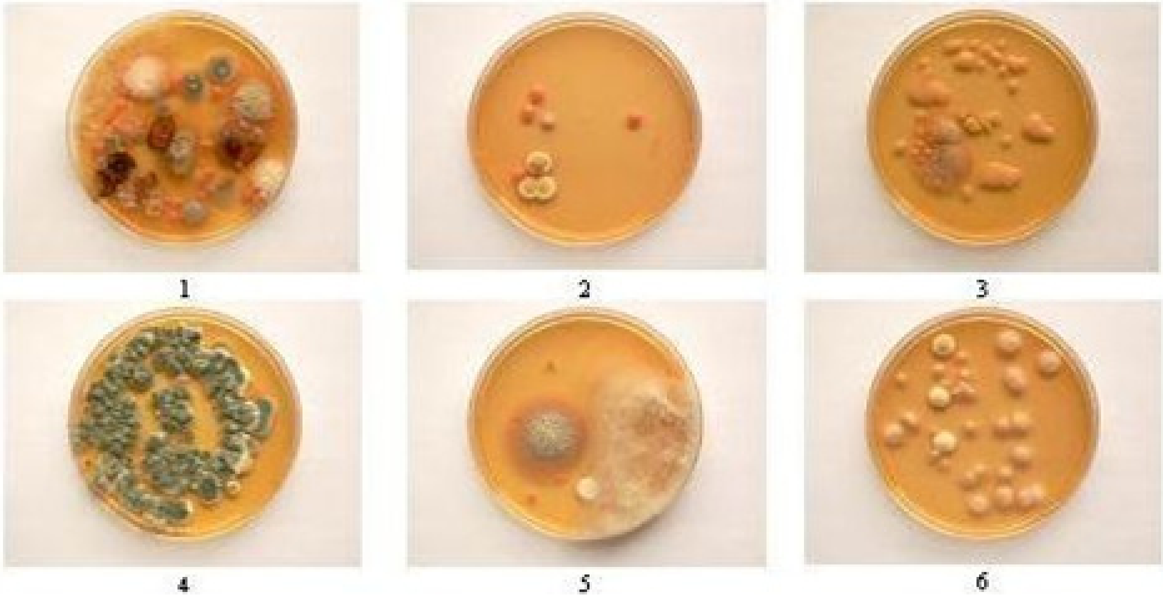


Fig. 2. Contamination of rain water with the propagules of microscopic fungi collected from steel plates coated with Zn chromated in different solutions after 1 year exposition to natural atmospheric conditions (Vilnius, Visoriai). Test solutions as in Fig. 1

Table 1. Concurrence of fungi species on steel plates coated with Zn chromated in different solutions after 1 year exposition to natural atmospheric conditions: a – fungi species collected from steel plates; b – fungi species collected from rain water

a							b						
Solution	1	2	3	4	5	6	Solution	1	2	3	4	5	6
1	/////						1	/////					
2	14	/////					2	27	/////				
3	42	11	/////				3	44	46	/////			
4	35	11	36	/////			4	12	17	13	/////		
5	29	13	32	16	/////		5	38	25	38	22	/////	
6	44	19	39	45	29	/////	6	30	13	33	12	19	/////

The data in Table 2 portray the specific composition of fungi, detected on the studied objects. Altogether on the plates studied there were detected microscopic fungi of 26 species during one year period, whose distribution depends on the external factors, especially on the substrate, in this case, on the passivation solution of Zn film.

3.2. Surface damage

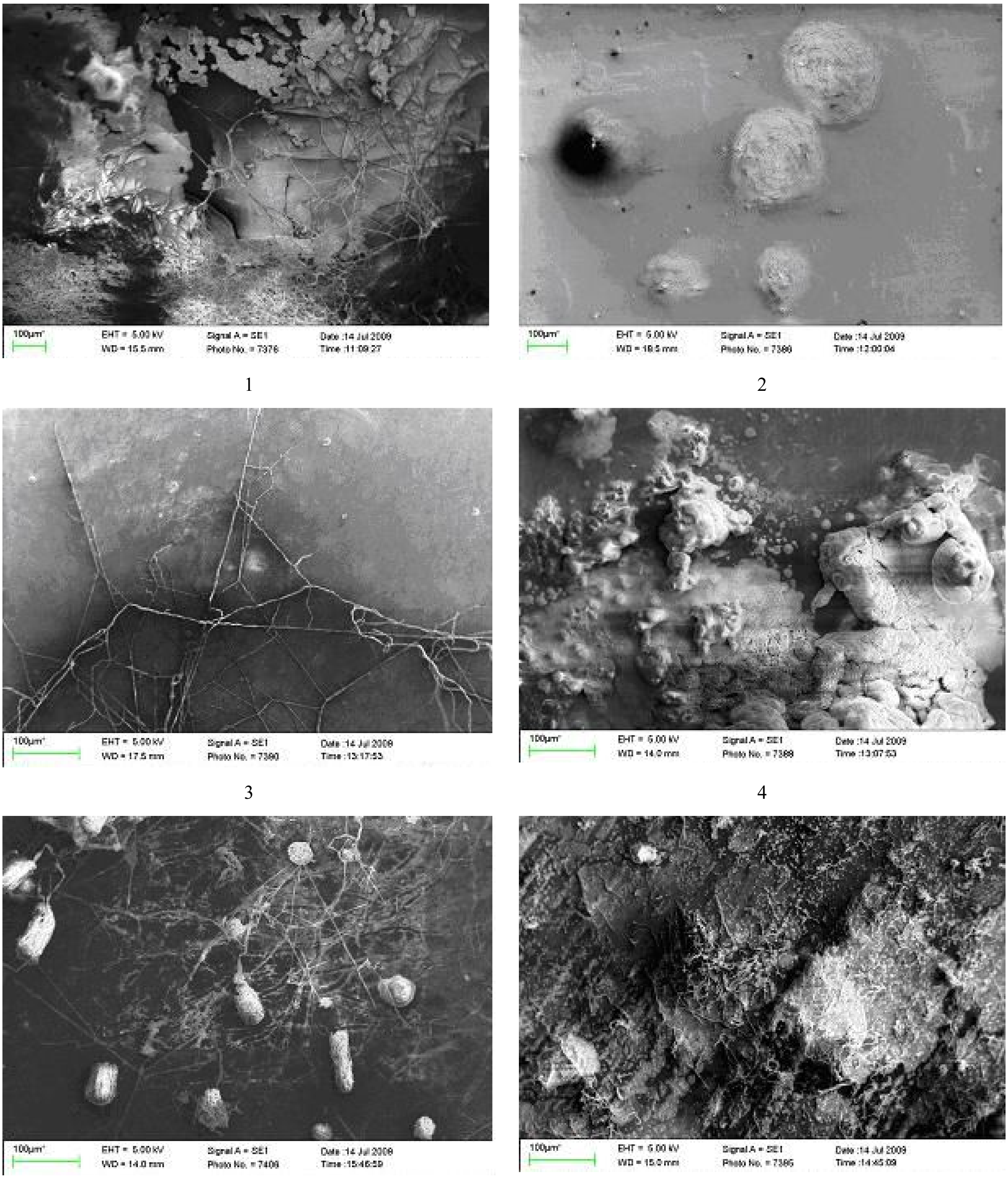
The data in Fig. 3 describe the effect of fungi on the surface of the studied steel plates, coated with the zinc coating chromated in various solutions. The surface of Zn coating passivated with the $Cr(NO_3)_3$ $9H_2O$ solution is cracked, cracks are clearly seen and hifes of fungi stretch over the surface. Oval fungi mycelium formations resembling the formation of crystallites on the plate surface and small centres of pitting corrosion are observed on the surface of steel plates coated with Zn and passivated in the $Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid solution (Figs. 3 – 2).

On the surface of steel plates coated with Zn and passivated in the Likonda 3Cr5 solution a scarse fungi mycelium and a slight film of crystallites is seen (Figs. 3 – 3). On the surface of passivated Zn coating deposited on a steel plate quite large crystallites and between them a cracked coating and steel surface are seen, as well as spread fungi colonies (Figs. 3 – 4). On the surface of steel and passivated Zn coating steel the growth of microscopic fungi and propagules of their conidiogenesis were

Table 2. Fungi contaminating steel plates coated with Zn chromated in different solutions after exposition to natural condition

Spiecies of fungy	1		2		3		4		5		6	
	P	V	P	V	P	V	P	V	P	V	P	V
Acremonium strictum									▓	▓		
Alternaria alternata							▓				▓	
Arthrinium phaeospermum	▓	▓					▓		▓		▓	
Ascotricha chartarum		▓								▓		▓
Aspergillus niger					▓					▓		
Aureobasidium pullulans		▓			▓	▓	▓		▓	▓	▓	▓
Beauveria densa						▓						▓
Candida albicans		▓							▓			▓
Chrysosporium merdarium	▓				▓	▓		▓			▓	
Cladosporium cladosporioides	▓				▓	▓	▓		▓		▓	
Cladosporium herbarum			▓			▓					▓	
Cladosporium sphaerospermum					▓	▓	▓					
Exopiala jeanselmei					▓						▓	
Fusarium moniliforme	▓		▓		▓	▓			▓		▓	
Fusarium spp							▓		▓		▓	
Paecilomyces parvus	▓										▓	
Penicillium decumbens	▓	▓										
Penicillium islandicum					▓	▓						
Penicillium spp.	▓	▓						▓				
Rhodotoruba rubra		▓		▓						▓		
Sclerotinia sclerotiorum					▓	▓			▓		▓	
Scopulariopsis brumtii	▓				▓	▓		▓				
Scytalidium lignicola					▓	▓	▓				▓	
Trichosporiella hyalina					▓	▓						
Verticillium alboatrum								▓			▓	
Verticillium album					▓	▓				▓		
Mycelia sterilia	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓

P – steel plate; V – raining water collected from steel plates.



1 2

3 4

5 6

Fig. 3. SEM images illustrating a general view of the surface of chromated plates in different solutions after 1 year exposition to natural atmospheric conditions (Vilnius, Visoriai). Test solutions as in Fig. 1.

observed. From these phenomena it can be believed that the solution can promote the growth of fungi and their conidiogenesis. On the surface of steel plates covered with Zn chromated in the Likonda 3Cr5 and paste solution a whitish film was formed, the surface became uneven in places cracked and coated with a crystallite film. The data obtained have shown that the microscopic fungi under the studied conditions are able to grow and promote the processes of crystallite formation and intensify the corrosion processes.

In order to elucidate the resistance of chromated zinc coatings to the influence of microscopic fungi the plates were kept for 60 days in contact with microscopic fungi, collected from analogous plates exposed to natural environmental conditions (Vilnius, Visoriai) for one year. The purpose of these studies was to determine the substances forming on the surface of the plates studied when they are in a direct contact with variuos microscopic fungi or their metabolites and other environmental factors. Here we present two graphical images illustrating the changes occuring on the plate surface. Fig. 4 presents the rentgenograms of the plate damaged by the action of fungi and environmental factors (Fig. 4, a, 1) and not damaged by fungi and environmental factors (Fig. 4, a, 2). The study was performed by applying the X-ray diffraction method, which allows directing of the ray at a grazing angle of 0.5°. The rentgenograms of surface of plates covered with fungi mycelium were obtained, and their comparison with those of analogous plates but without any influence of fungi and environment suggests that on the surface of chromated Zn plates $ZnCO_3(OH)_6 \cdot H_2O$ (PDF 11-287) crystallite with a size of 10 nm and a bare handful of $Zn_5(CO_3)_2(OH)_6$ (PDF 19-1458) are formed under the action of fungi and environmental conditions (Fig. 4, b).

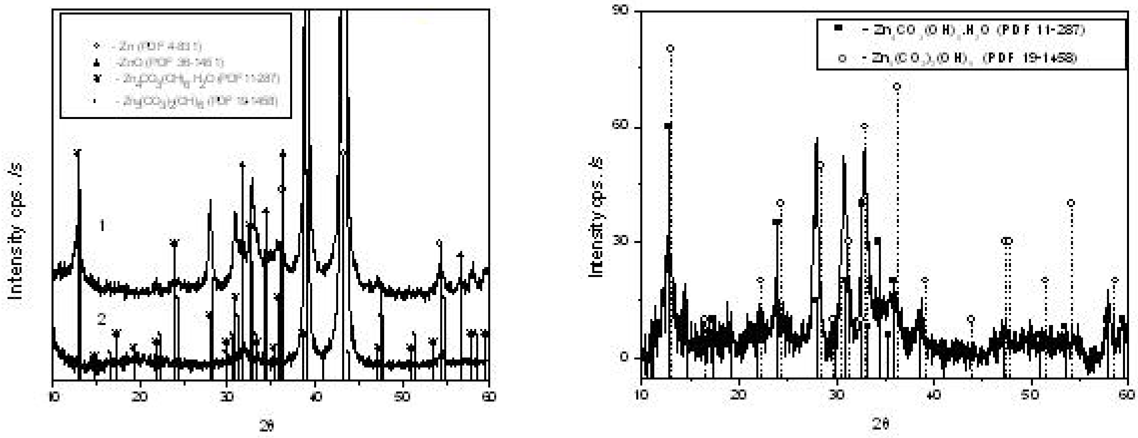
This coincides with the data obtained by other authors Pérez Néstor (2004) [15] who note that after atmospheric corrosion in Zn can corrode forming “white rust” in fact the compound $Zn_4CO_3(OH)_6$ or $ZnCO_3 \cdot 3Zn(OH)_2$ is zinc carbonate or “white rust” or wet storage stain (porous). According to Pérez Néstor (2004) furthermore of uniform corrosion can be accomplished be selecting an adequate: 1) material having a uniform microstructure 2) coating or point 3) inhibitors for retarding or supressing corrosion. These are classified as adsorption – type hydrogen – evolution poisons, seawengers, oxidizers and vapor-phase 4) cathodic protection, which is an electrochemical process for suppressing of corrosion in large steel structures.

The different oxidation states of chromium and reactive oxygen species (ROS) generated in redox reaction with chromium ions are presented and characterized by Poljsak et al [16].

It should be mentioned that the X-ray diffraction method did not allow determining quantitatively the Zn salts formed and their ratio because of uneven coverage of the plate surface with fungi mycelium and salt crystallites. However, it can be stated that on Zn coatings chromated in different solutions and on steel substrate crystallites of Zn salts of the same composition were formed. When a rentgenogram was recorded a site most affected by fungi that is where “white rust” consisting of $ZnCO_3(OH)_6 \cdot H_2O$ and $Zn_5(CO_3)OH_6$, was accumulated, it became clear that the ratio of these compounds is approximately 3 : 1.

The data presented in Table 3 suggest that just the 48 hours exposure in the stepped-up salt fog chamber has a significant influence on the looks of the conversion films of patterns, treated in different passivating solutions. The conversion films formed on the zinc surface using simple Cr(III) solutions were most changed. One can observe significant red (Fe) corrosion of the patterns (Table 2). The full corrosion of the patterns, coated with zinc and passivated in the solution was observed after its exposure to the stepped-up salt mist chamber.

Meanwhile, only an inconsiderable red corrosion of conversion films, formed using elaborate commercial



a

b

Fig. 4. XRD patterns for zinc coated plates: a: 1 – the plate surface subjected to the action of environment and fungi mycelium; 2 – the plate not subjected to the action of humidity and fungi mycelium (auditorial); b – XRD patterns for zinc coated plate surface area (collection of white sediments) the most affected by the action of environment and fungi mycelium. The pattern was measured by the grazing incidence method

Table 3. The corrosion resistance of different passivated 9 micron thickness zinc patterns, placed in the salt fog chamber

Type of passivation	Arieal of corrosion (A %)				
	48 h test	72 h test	192 h test	328 h test	382 h test
$Cr(NO_3)_3 \cdot 9H_2O$	2.5<A<5	50<A			
$Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid	No defects	No defects	2.5<A<5		
Li 3 Cr 5	No defects	No defects	No defects	No defects	No defects
Li 3Cr V	No defects	No defects	No defects	0< A< 0.1	0.1< A< 0.25
Li3 Cr MC	No defects	No defects	No defects	No defects	0< A< 0.1
Li3 Cr 5 + paste*	No defects	No defects	No defects	No defects	0.1< A< 0.25

* Paste: 14 ml $Cu(NO_3)_2 \cdot 3H_2O$ + 66 ml $FeCl_3 \cdot 6H_2O$ + 20 ml NH_4Cl + 60 g kaolin.

solutions (Likonda 3Cr5, Likonda 3CrV, Likonda 3Cr MC), which contain organic and inorganic Cr(III) acid complexes, as well as a supplement of Co^{2+}, F^{-}, SO_4^{2-} ions, were observed only after its exposure for 382 hours in the salt fog chamber. Evidently, in the conversion films, formed using the solutions containing Co^{2+}, F^{-}, SO_4^{2-} ions, Cr(III) ions are faster oxidized to Cr(VI) under atmospheric conditions by oxygen during the stepped-up corrosion tests.

The data obtained show that microscopic fungi are an active factor of atmospheric corrosion of steel and other metals. This is partly confirmed by the data obtained by other authors [16].

4. CONCLUSIONS

1. Metal atmospheric corrosion processes are conditioned by the multitude of external factors, among which an important place should be given to microscopic fungi, which are widely spread in the places of metal exploitation and often can become the cause of initial corrosion and determine its behaviour.

2. Organic contaminants present on the surface of steel plates coated with Zn coatings chromated in different solutions promote functioning of microscopic fungi, which find their way to the metal surface together with dust settlement.

3. Microscopic fungi start their activity and excret various metabolites, which damage the surface of steel plates coated with the Zn coating and the surface gradually covers with white rust, consisting of $Zn_4CO_3(OH)_6 \cdot H_2O$; $Zn_5(CO_3)_2(OH)_6$ salts crystallites, which determine further corrosion behaviour.

4. By employing various methods for evaluation of steel surface resistance to microscopic fungi it has been determined, that a mixture of the chromium compound $Cr(NO_3)_3 \cdot 9H_2O$ + malonic acid can diminish the damage of metal surface which is under action of some fungi mixtures, for instance, (*Alternaria alternata* + *Aspergillus penicillloides* + *Geomyces pannorum* + *Cladosporium herbarum* + *Penicillium carneum)*. The results obtained can be the basis for further investigations and practical implementation, but the sensibility of this compound to moisture should be beared in mind, inasmuch as the resistance (R_P) of the zinc coating chromated in this solution being exposed to the salt fog chamber without fungi markedly decreases.

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