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INFLUENCE OF MITOSPORIC FUNGI UPON ZINC-POLYMERIC COATINGS ON STEEL UNDER THE DIFFERENT ENVIRONMENT

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Abstract. Zinc-polymeric coating samples were exposed to different environmental conditions (for 2 years): marine – dunes on the shore of the Baltic Sea (Neringa), rural-agrarian district of Moletai and the industrial zone of Vilnius. During the whole period of the study 94 species of fungi, were isolated from the exposed samples of zinc-polymeric coating on steel. The zinc-polymeric coatings exposed to marine and rural-agrarian environments were deteriorated most markedly. A scanning electron microscope (SEM) was used to characterize the morphology of the surface. The phase composition of the zinc-polymeric coatings on the steel substrate was analysed by an X-ray diffractometer (XRD). The products formed on the zinc-polymeric coatings were detected by a Fourier transformation infrared spectrometer (FTIR). The effect of environmental conditions on the mass change of the samples was determined by the standard dissolution method.

Keywords: zinc-polymeric coating, steel, mitosporic fungi, environmental impact, changes of surface, corrosion.

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Introduction

It has recently been stated, that approximately 40–50% of materials damage in the environment is connected with the activities of microorganisms, while in oil industry this index is up to 77% (Krylenkov *et al.* 2003). Such a value is determined by the environmental conditions. Processes caused by microorganisms occur in various objects (Diaz-Ballote, Ramanauskas 1999; Huang *et al.* 2006). Microorganisms deteriorate different elements inside and outside the objects, both constructive and functional (Helsen, Breme 1998; Beech 2004; Li *et al.* 2004). An active fungi growth is observed in municipal utilities, various tunnels, underground crossings, collectors, wooden, stone, metallic and multicomponental buildings and equipment, railroads and other means of transport (Hughes, Poole 1989; Roberge 1998; Marcus, Oudar 2002). The activity of microorganisms depends on their biological variety in the environment, their action specificity and ability to adapt to extreme natural environment, as well as on the composition of the unusual substrates which are formed by contamination with microorganisms and coupled with the surrounding medium (Ramanauskas *et al.* 1998, 2000, 2005; Narkevičius *et al.* 2003). Technical objects are deteriorated by bacteria, mitosporic fungi and other biota as well as their communities. The products of their activity (acids, alkalis, enzymes) and a variety of other aggressive chemical compounds soon start to contact with the components of the affected object, new chemical compounds are formed, which integrate into the destruction processes and accelerate further deeper and more diverse processes (Barton 1976; Lee *et al.* 2007; Lichušina *et al.* 2008). It should be mentioned, that small microorganisms possess vast possibilities of surface contact with the medium, which determines their destruction capability. The majority of microorganisms under natural conditions can survive for a long time in the anabiosis state and pass into an active performance only when the relative humidity of the medium reaches 60% and that of the substrate (constructions, walls, etc.) exceeds 50%. Under such conditions their performance becomes an aggressive destructive factor which can

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damage metallic constructions and become a threat for human health and other biota. Microbiological disturbance is promoted by the changes in temperature and medium pollution with nitrogen compounds, sulphur, carbon monoxide and dioxide, chlorides and soot, which are initially used by microorganisms for their nutrition (Domsch *et al.* 1980; Hughes, Poole 1989; Lugauskas *et al.* 2002; Marcus, Oudar 2002).

Means to limit, stabilize or completely suppress the disturbances caused by microorganisms have been searched (Ignatev, Mikhailova 1987). The surfaces of metallic constructions or equipment damaged by microorganisms get chapped and exfoliate. Their hardness and lifetime markedly diminish. Under such conditions growing mitosporic fungi are detected on metals, and the variety of them determines the corrosion behaviour (Yang *et al.* 1996). To protect metals from damage caused by microorganisms, polymeric films have been investigated (Bierwagen 2008; Binkauskienė *et al.* 2009). Recently much attention has been devoted to studies of zinc-polymeric coatings, which are widely used in automotive industry and to protect railway transport, large-block buildings, bridges and other objects made of steel to protect them from corrosion and mechanical damages (Kikuchi, Streekumari 2002; Marchebois *et al.* 2002; Tüken 2006). These coatings are composed of metallic zinc and a polymer mixture and protect from corrosion in the same manner as does the zinc coating obtained by galvanic zinc deposition. Zinc interacts with the metal surface forming a homogeneous protective film (Marchebois *et al.* 2004; Jagtap *et al.* 2007).

The aim of the present study was to isolate and identify mitosporic fungi detected on the zinc-polymeric coating deposited on steel to determine their importance in the injury processes occurring in the different ecological environments.

1. Materials and methods

Steel plates 10×15 cm and 1×3 cm in size and up to 1 mm in thickness coated with the zinc-polymeric film Dinitrol 443 L Zinkfarbe (made in EFTEC Aftermarket GmbH Pyrmonterstr 76 D-32676 Lügde) were used for studies. The density is 500 g/m^2 at a coating thickness of 100 µm. The thickness of coatings used for testing was 100 ± 15 µm. The thickness of coatings was measured by using a magnetic thickness meter MT-41NC. The thickness of every specimen was measured in 9 different points of the coating.

The zinc-polymeric coatings were obtained by paint working. The zinc-polymeric coating samples were exposed to different environmental conditions (for 2 years): marine (M) – dunes on the shore of the Baltic Sea (Neringa), rural-agrarian (R) – Kulioniu village in district of Moletai and the industrial (I) zone of Vilnius. The investigation sites were installed according to the requirements of ISO 8565:1992(E) standard. At every climatic study ground 15 steel plates were studied. The reference sample not contaminated with fungi zinc-polymeric samples were exposed under standard conditions (The Law of Lithuanian Government, HN-69: 2003). Mitosporic fungi from steel plates covered with the zinc-polymeric coating were isolated after 0.5, 1.0, 1.5 and 2.0 years of exposure. Two nutrient media were used for fungi isolation: standard malt agar (DIFCO) and dichloranglycerol agar (DG – 18, OXOID). The media were sterilized for 15 min by autoclaving at 121 °C. The zinc-polymeric coatings on steel after exposure were put straight on the agar medium for direct dissociation from the substrate (steel and silica glass plates covered with the zinc-polymeric coating). Microorganisms were transferred from the coating surface to the agar nutrient media with a sterile eyelet, a hook, a sterile pad or directly by the application method.

In order to isolate mitosporic fungi developing or present on the zinc-polymeric coating surface the samples were put in Petri dishes filled with a sterile agar medium of malt extract supplied with chloramphenicol (50 mg/l). After that the medium with the samples was sown up and cultivated in a thermostat at a temperature of 26 ± 2 °C. The extent of fungal growth was assessed by the naked eye and by a light microscope MVS-10 (Russia).

The processing of the initial data was performed using the modified methods (Booth 1971; Mirchink 1988; Bondartseva 2012). Average means of 378 assays are presented in the paper, taking 126 assay from the each environment (marine, rural-agrarian and industrial).

The changes in the surfaces of the zinc-polymeric coating were recorded using both a SEM EVO 50 EP (Carl Zeiss, SMTAG, Germany) and a light microscope MVS-10 (Russia).

The isolates were ascribed to taxonomic groups according to Ainsworth and Bisby's Dictionary of fungi (Hawksworth *et al.* 1995; Kirk *et al.* 2004). Fungi were identified according to various manuals (Carmichael *et al.* 1980; Chaverri, Samuels 2003; Domsh *et al.* 1980; Gams 1971; Klich 2002; Kozakiewicz 1989; Lugauskas *et al.* 1987, 2002; Nelson *et al.* 1983; Ramirez 1982; Samson, Frisvad 2004; Samson 1974; Oorschot 1980).

A Nicolet model 5700 FTIR in conjunction with a 10 Spec (10 Degree Specular Reflectance Accessory) was used for spectroscopy investigations of corrosion products on investigated samples. Reflectance spectra of samples were obtained in the reflectance mode. In all cases the spectral range was 4000–400 cm^{-1} (reciprocal wave length) with a 4 cm^{-1} resolution and 64 scons. Spectral manipulation included baseline correction, removal of carbon dioxide absorption bands and subtraction of water vapour interferences. The investigated samples of the zinc-polymeric coating were cleaned with dry filter paper. The atmospheric corrosion products formed on the zinc-polymeric coating surface were eliminated, collected and their FTIR spectra were recorded. In this way the products formed by a biological agent were detected.

The phase composition of the coating on the steel substrate was analysed by an XRD DRON – 3.0 Cu K_α ($\lambda = 0{,}154$ nm, U = 30 kV, I = 20 mA) without any additional proportions.

The mass change of coating was determined by the following method: prior to exposure coatings (plates) were washed with deionised water, dried in the air, 24 hours kept in an excicator with P_2O_5 (phosphorus pentoxide), then they were weighed. The same procedure was repeated after exposure of samples (after 0.5, 1.0, 1.5 and 2.0 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 8407:2009 standard: a) exposing for 3 min to 100 g/l CH_3COONH_4 (ammonium acetate) solution at a temperature of 70 °C; b) washing with deionised water; c) drying in an excicator with P_2O_5 for 24 hours; d) weighing.

2. Results and discussion

2.1. Contamination of zinc-polymeric coatings on steel by mitosporic fungi

Fungi have important biogeochemine roles in the biosphere and are intimately involved in the cycling of elements and transformations of both organic and inorganic substates. Fungi are major agents of the biodeterioration of plaster and other material (Lugauskas 1997; Gadd 2007). Little and Stahle (2001) found the chemical composition and the quantity of adsorbed organic materials were strongly depended on the nature of the substratum.

Various ecological environments were chosen for metal exposure in order to elucidate their impact on steel coating and to determine the variety of mitosporic fungi in the medium, to which the zinc-polymeric coatings were exposed. Table 1 presents average yearlong meteorological and air pollution data obtained in different environments.

From Figure 1 it is seen that zinc-polymeric coatings on steel exposed to all the conditions are contaminated with propagules of mitosporic fungi, from which fungi of various species begin to develop under favourable conditions. After the studies and identification by using the mentioned methods of fungi isolated from the zinc-polymeric coatings on steel it has been found that a part of fungi species are present on the coatings exposed to all the mentioned environmental conditions (Fig. 2). From the data presented in Figure 2 it is seen that the greatest variety of propagules detected on the zinc-polymeric coatings on steel belongs to *Cladosporium cladosporioides* fungi (M – 58; R – 73; I – 51%, respectively); *C. herbarum* (M – 32; R – 36; I – 48%); *Alternaria alternata* (M – 32; R – 43; I – 14%); *Acremonium strictum* (M – 23; R– 38; I – 27%); *Paecilomyces parvus* (M – 21; R – 63; I – 23%); *Penicillium brevicompactum* (M – 63; R – 14; I – 13%); *P. chrysogenum* (M – 21; R – 19; I – 27%); *P. verrucosum* (M – 26; R – 11; I – 22%). The frequency of detection of some fungi at different exposure sites differed markedly: *Penicillium olsonii* (M – 14; R – 2; I – 6%); *Sporotrichum aurantiacum* (M – 28; R – 7; I – 13%); *Ulocladium chartarum* (M –14; R – 8; I – 21%); *Alternaria tenuissima* (M – 3; R – 16; I – 29%); *Arthrinium phaeospermum* (M – 3; R – 22; I – 38%); *Oidiodendron echinulatum* (M – 8; R – 29; I – 16%). It has been observed that in the industrial environment where a lot of pigeons, sparrows and other birds fly most often thrush fungi are detected: *Candida albicans* (M – 1; R – 21; I – 32%); *Rhodotorula rubra* (M – 6; R – 10; I – 23%); *Exophiala jeanselmei* (M – 2; R – 6; I – 17%), *Asperlillus fumigatus* (M – 6; R – 13; I – 49%) and *Eurotium repens* (M – 3; R – 11; I – 23%). In all variants of experiments a sterile mycelium mostly of white and reddish colour is abundant on the zinc-polymeric coating (M – 89; R – 73; I – 84%).

19 species were found in the marine environment, but not in the other 2 environments. The following fungi can be considered as characteristic for marine conditions: *Blastabotrys nivea* (the frequency of detec-

Table 1. Average yearlong meteorological and air pollution data obtained in different environments

Environment	Parameters					
	Temperature, °C	Number of sunny days H/years	Amount of precipitations, mm/years	Wind speed, m/s	SO_2 concentration, μg/m^3	NO_2 concentration, μg/m^3
Marine	~ 7.0–7.5*	1850–1900*	700–750*	5.5–6.0	0.04–2.29**	0.44–4.24**
Rural-agrarian	~5.5–6.0*	1650–1700*	650–700*	3.0–3.5	~4.0–4.6***	11–12***
Industrial	~ 6.4*	1650–1700*	700*	3.5–4.0	~ 1–3***	22–30***

*Lithuanian Hydrometeorological Service
**Institute of Physics (2007)
***Office of environment protection of Lithuania

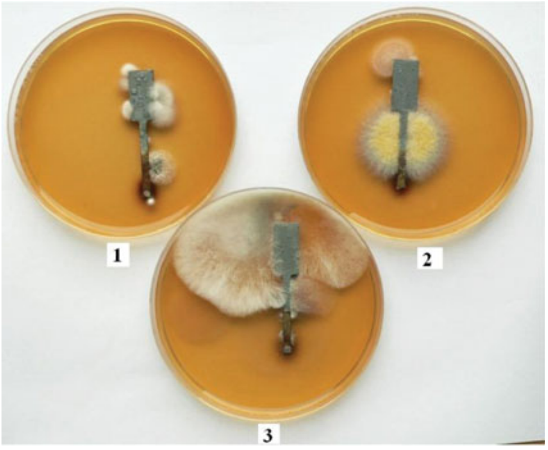

Fig. 1. Contamination with mitosporic fungi of the zinc-polymeric coatings on steel, exposed for one year to different environments: 1 – marine; 2 – rural-agrarian; 3 – industrial

tion 21%), *Fusarium solani* (19%), *Chaetomium globosum* (16%), *Penicillium atramentosum* (16%), *Acremonium murorum* (14%), *Diplococcum spicatum* (14%), *Chrysosporium pannicola* (13%), *Penicillium mirczynskii* (11%). The frequency of detection of other fungi did not exceed 10% (Table 2).

From the zinc-polymeric coatings on steel exposed to the rural-agrarian environment, alongside the fungi mentioned in Figure 2, mitosporic fungi of 20 species were isolated which were not detected under other environmental conditions. The following fungi species can be considered as the predominating ones under the conditions of agrarian environment: *Penicillium lanosum* (the frequency of detection 36%), *P.cyclopium* (34%), Sporotrichum olivaceum (29%), *Verticillium alboatrum* (24%), *Gilmaniella humicola* (21%), *Myceliophthora vellerea* (21%), *Penicillium godlewskii* (21%).

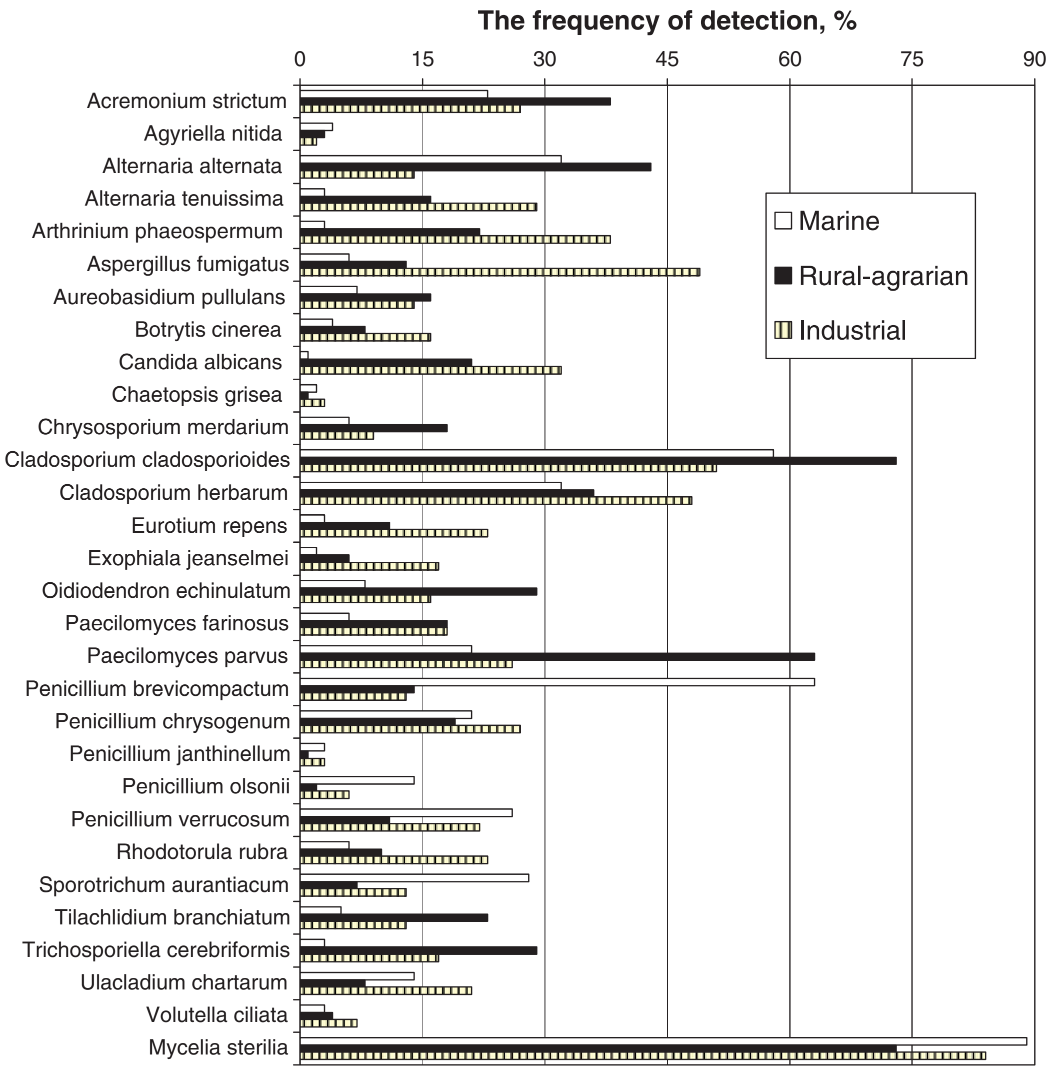

Fig. 2. Mitosporic fungi detected on the zinc-polymeric coatings on steel exposed for 2 years to different environments

Table 2. Mitosporic fungi isolated from the zinc-polymeric coatings on steel exposed to only one type of environmental conditions for 2 years

Environment	The isolated fungi and their frequency of the highest detection, %
Marine	*Acremonium domschii* – 6; *A. murorum* – 14; *Blastabotrys nivea* – 21; *Chaetomium globosum* – 16; *Chrysosporium pannicola* – 13; *Dennisographium episphaeriae* – 1; *Diplococcium spicatum* – 14; *Fusarium avenaceum* – 2; *F. moniliforme* – 8; *F. poae* – 14; *F. sambucinum* – 3; *F. solani* – 19; *F. sporotrichioides* – 1; *Heterocephalum aurantiacum* – 1; *Mortierella polycephala*– 3; *Penicillium atramentosum* – 16; *P. miczynskii* – 11; *Sphaeridium candidum* – 1; *Sphaerulomyces coralloides* – 2.
Rural-agrarian	*Alternaria dianthi* – 18; *Amblyosporium botrytis* – 7; *Chrysosporium olivaceum* – 3; *Fusarium oxysporum* – 13; *Gilmaniella humicola* – 21; *Minimidochium setosum* – 8; *Mortierella hyalina* – 14; *Myceliophthora vellerea* – 21; *Parapericonia angusii* – 18; *Phaeostalagmus cyclosporus* – 7; *Penicillium cyclopium* – 34; *P. godlewskii* – 21; *P. lanosum* – 36; *P. nalgiovense* – 15; *Sarcopodium tortuosum* – 9; *Sarocladium oryzac* – 16; *Scopulariopsis brumtii* – 11; *Sporotrichum olivaceum* – 29; *Thallospora aspera* – 10; *Verticillium alboatrum* – 24.
Industrial	*Acremonium humicola* – 10; *Acrophialophora fusispora* – 7; *Blastomyces dermatitidis* – 6; *Calcarisporium arbuscula* – 14; *Ceratocystis olivacea* – 12; *Chrysosporium pannorum* – 23; *Cochlonema megalosomum* – 17; *Curvularia lunata* – 15; *Fulvia fulva* – 34; *Geotrichum candidum* – 18; *Honsfordia ovalispora* – 12; *Michenera artocreas* – 3; *Mucor racemosus* – 21; *Oidiodendron tenuissimum* – 39; *Paecilomyces niveus* - 17; *Pagidospora amaebophila* – 3; *Phoma exigua* – 16; *Phymatotrichum funigicola* – 7; *Penicillium funiculosum* – 31; *P. nigricans* – 17; *P. sclerotiorum* – 12; *Rhizomucor pusillus* – 27; *Sclerotinia sclerotiorum* – 29; *Trichoderma polysporum* – 17; *Tubercularia vulgaris* – 8.

The biggest variety of the species of mitosporic fungi was detected on the steel specimens covered with the zinc-polymeric coating exposed to the industrial environment. 25 species of mitosporic fungi which were isolated and identified here were not found under any other environmental conditions. Here the following fungi species dominated: *Oidiodendron tenuissimum* (the frequency of detection 39%); *Fulvia fulva* (34%); *Penicillium funiculosum* (31%); *Sclerotinia sclerotiorum* (29%), *Rhizomucor pusillus* (27%), *Chrysosporium pannorum* (23%), *Mucor racemosus* (21%). The frequency of detection of other fungi species did not exceed 20%. The specific contamination of the exposure site, where organic and other non-specific contamination components are abundant can be inferred by the composition of the isolated fungi species.

It can be concluded that, the zinc-polymer coating is not a strong biocide and does not prevent the growth and formation of bioagents on its surface.

Some sorts of fungi were detected on various metals at environmental conditions by other authors (Little, Stahle 2001; Videla, Herera 2009). Therefore one can agree with Videla and Herera, that most of fungi can synthesize and emit in the environment various organic acids. The elucidation of the action of collected fungi enables to implement the means for corrosion control (Videla, Herera 2009).

2.2. The changes in the surfaces of zinc-polymeric coatings on steel

The changes in the surfaces of the zinc-polymeric coatings on steel after certain exposure time under the above mentioned conditions (Fig. 3) were established by the micrographic method.

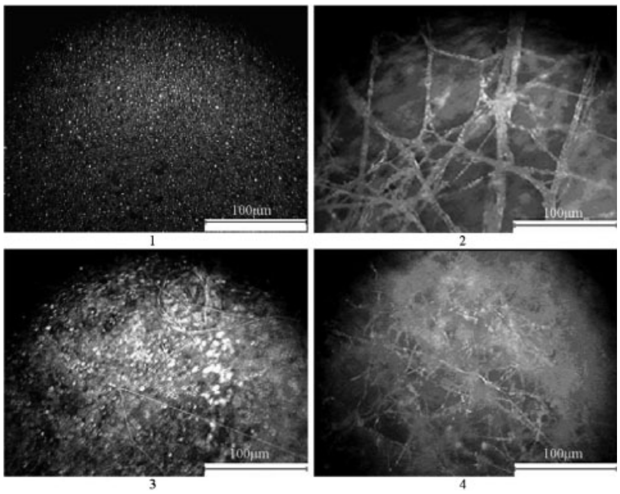

Fig. 3. Micrographs of zinc-polymeric coatings on steel under different environment conditions: 1 – reference (not exposed); 2 – marine; 3 – rural-agrarian; 4 – industrial

In Fig. 3–1 the image of reference sample is shown. As it was expected, the morphology of the coating surface was hardly changed and had a view of a fine-grained structure with a grain size of 1–5 μm. In Fig. 3–2 a micrograph of sample exposed to the marine environment is shown. On the surface of the sample a thick layer of mycelium-like structure is formed. The thickness of layer is ~10–15 μm, the width and length of the layer vary from ~100 to 200 μm. In Fig. 3–3 a micrograph of zinc-polymer sample exposed to the rural-agrarian environment is shown. In this case, the surface is covered with mycelium-like wires and particles of ellipse form, which chaotically cover the whole surface of the sample.

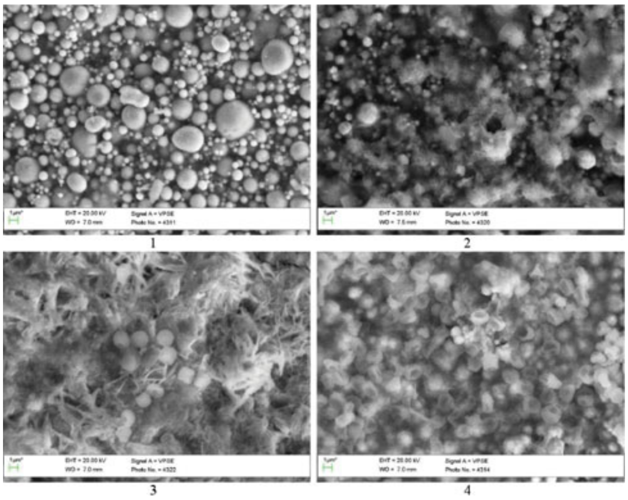

Fig. 4. The changes in the surfaces of zinc-polymeric coatings on steel after 1.5 years of exposure to different environment conditions: 1 – reference (not exposed); 2 – marine; 3 – rural-agrarian; 4 – industrial

The diameter of wires does not exceed 1–2 μm, and the ellipse-like particles diameter varies from 3 to 5 μm. In Fig. 3–4 a micrograph of the sample exposed to the industrial environment is shown. In this case the surface is covered with mycelium wires and clusters.

The SEM method made it possible to analyse surface changes, related to biocorrosion deterioration in the micrometer diapason. Figure 4 presents pictures of the surface of the zinc-polymeric coatings on steel plates exposed for 1.5 years to the marine, rural-agrarian and industrial environments.

After 1.5 years from the beginning of the experiments the surface of the zinc-polymeric coatings exposed to all the climatic conditions was damaged to a variable degree: somewhat deeper and rarer ones in the marine environment, thicker and non-uniform ones – in the other zones. Grooves were on the surface, engraved by bends of various shape and 2–4 μm in size. After 2 years of exposure on the surface of the zinc-polymeric coatings on steel developing fungi formed conidia, forming organs and started to intensively develop and spread, the deterioration of the polymeric coating became more intensive (Fig. 5). This was most clearly seen on the zinc-polymeric coatings exposed to the industrial environment, where phialospores (conidia borne on phialides) of the formed conidia of *Aspergillus fumigatus* fungi were clearly seen. On the analogous zinc-polymeric coatings specimens exposed to the marine environment the fungi of *Cladosporium cladosporioides* species developed most intensively, forming on the surface of the coating deep holes of similar size. The surface of the zinc coatings exposed to the rural-agrarian environment was covered with a rather thick fungi mycelium reminiscent of a cobweb. Clearly formed organs of propagation were not observed after 1.0 year of exposure.

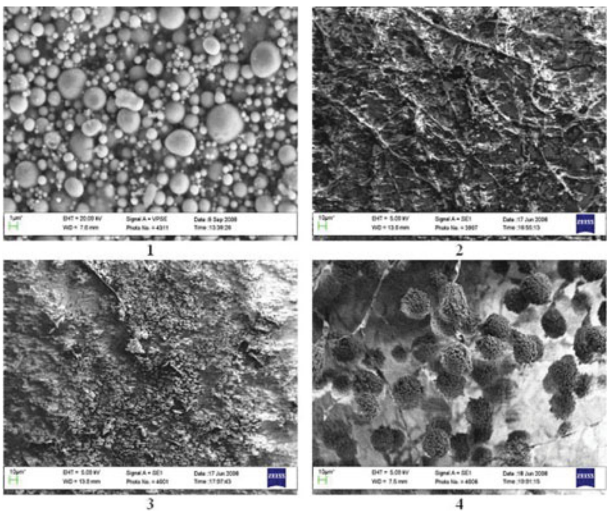

Fig. 5. A general view of mitosporic fungi development on the surfaces of zinc-polymeric coatings on steel after 2 years of exposure under different environment conditions: 1 – reference (not exposed); 2 – marine; 3 – rural-agrarian; 4 – industrial

On a part of specimens covered with the zinc coatings an almost continuous mucous bloom was seen which was formed by developing yeast-like fungi: *Exophiala jeanselmei*, *Rhodotorula rubra*, *Aureobasidium pullulans*.

2.3. Results of spectroscopy investigations of the zinc-polymeric coatings on steel

In Figure 6 FTIR reflection spectra of reference samples of zinc-polymer coatings (1) and coatings exposed to the marine, rural-agrarian and industrial environments are shown.

There is only one absorption peak at a wavelength of 580 ± 2 cm^{-1} seen in the spectrum of reference sample, though, the spectrum of product 2 is almost identical to the spectrum of product 3, where the peaks

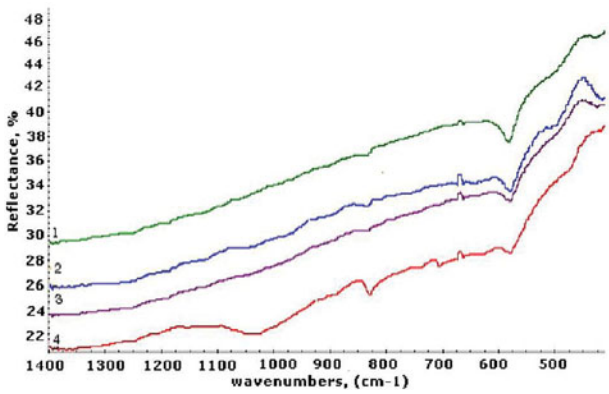

Fig. 6. Results of FTIR spectroscopy investigation of corrosion products on the zinc-polymeric coatings under different environment conditions: 1 – reference (not exposed); 2 – marine; 3 – rural-agrarian; 4 – industrial

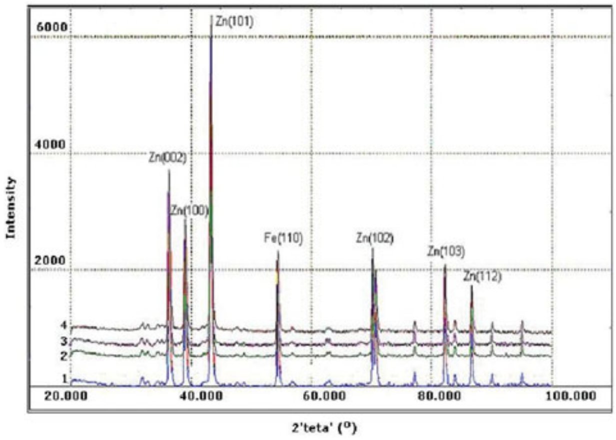

Fig. 7. Phase composition of coatings determined by XRD method under different environment conditions: 1 – reference (not exposed); 2 – marine; 3 – rural-agrarian; 4 – industrial

at wavelengths of 1150 cm^{-1}, 829,2 cm^{-1} and 662,2 cm^{-1} are almost identical in both cases, and also the shift to 578 cm^{-1} wavelength is visible in the spectra of both samples. Vibration differing from the reference spectrum may be ascribed to the vibration from bioagents. An increase in complexity of vibration spectrum of sample 4 may be explained by the complexity of bioagents and additional atmospheric pollution due to the weather conditions in the industrial environment.

Our data, which deals with the changes in zinc polymeric coatings on steel surface, does not fully agree with the data of similar investigations of other authors (Little, Stahle 2001). It can be explained by the fact, that in our tests the metal was coated with the zinc polymeric coating resistant to fungi metabolites.

In Figure 7 XRD spectra of all four samples of zinc-polymer coatings are shown. As it is visible from the spectra, the elements detected are Zn and Fe. All four zinc-polymeric coatings did not undergo phase transitions, there are almost no peaks of zinc oxide. The changes in morphology of the surface seen in Figures 4 and 5 do not necessarily lead to the changes in XRD difractogram, the effect of the bioagent may be not sufficient for the emergence of the mentioned changes, inasmuch as the XRD analysis shows the changes in the material structure and emergence of a new phase identified by the XRD method.

2.4. Mass changes of zinc-polymeric coatings

Steel plates 10 × 15 × 1 cm in size coated with the zinc-polymeric film were used for studies. The effect of mitosporic fungi and other factors on the zinc-polymeric coatings under different exposure conditions could be inferred by the changes in coating mass occurring during certain exposure time (Table 3).

Table 3. Mass changes of zinc-polymeric coatings (g/m^2) depending on the duration of exposure

	Duration of the exposure (year)			
Environment	0.5	1.0	1.5	2.0
Marine	10.1	–	13.0	3.2
Rural-agrarian	7.4	2.6	2.6	8.3
Industrial	1.2	2.0	3.2	2.1

The mass change (increase) of zinc-polymeric coatings (g/m^2) depending on the duration of exposure (Table 3) shows that at the different stations and different exposure time the tendency of unequal variation in mass is observed. This can be explained not only by the corrosion of the protective coating, but also by the removal of corrosion products due to the atmospheric impact and the activity of mitosporic fungi. As seen from the meteorological data presented in Table 1, merely greater windiness in the marine atmosphere leads to more frequent wetting and drying of the surface, as well as more frequent washing of the corrosion products from the surface of zinc-polymeric coating. During the year with moister conditions the corrosion rate does increase, corrosion products are easier cleaned away by atmospheric precipitation, whereas the decrease in coating mass and the decrease in total loss could be compensated by the activity of the mitosporic fungi present in the coating.

Mass losses of zinc-polymeric coatings (g/m^2) after removal of corrosion products depending on the exposition duration and location (Table 4), the tendency of corrosion rate does increase by increasing on the duration of exposure. The red corrosion of Fe in the marine environment was observed after 1.5 years of exposure, while in the industrial and rural-agrarian environment red corrosion is still not observed. The highest corrosion rate of Zn polymeric coating is observed in the marine environment, and the minimal one in the industrial environment.

In order to better understand the nature of deterioration processes occurring in coatings under different environment conditions and their dependence on the alternation of meteorological conditions the data obtained are shown in the diagram form (Fig. 8).

Table 4. Mass losses of zinc-polymeric coatings (g/m^2) after removal of corrosion products depending on the duration of exposure

	Duration of exposure (year)			
Environment	0.5	1.0	1.5	2.0
Marine	27.0	24.0	30.3	33.7
Rural-agrarian	24.7	15.3	25.5	33.7
Industrial	16.4	17.8	20.9	11.1

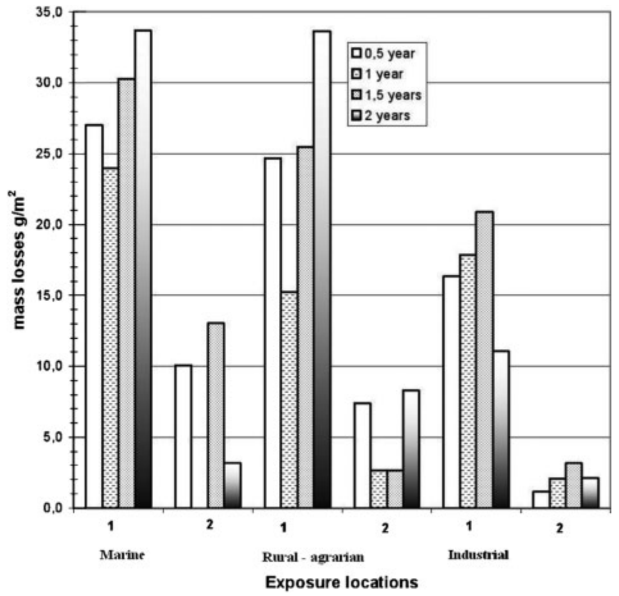

Fig. 8. Mass losses (1) after removal of corrosion products and mass change (2) after exposure of zinc-polymeric coatings versus the duration of exposure

Figure 8 presents the mass loss after 2 years at the exposure sites and the quantity of the corroded zinc in the exposed coatings, which was determined by the standard dissolution method.

Conclusions

1. Under the conditions of polluted environment mitosporic fungi are an active biological factor capable of functioning on the surface of zinc-polymeric coating and thus promote or suppress the deterioration processes occurring on it with the help of the secreted metabolites and gradually become one of the reasons of metal corrosion.

2. The zinc-polymeric coatings were contaminated with mitosporic fungi of different species. Fungi of 30 species were detected on all the specimens exposed for 2 years. Other fungi detected on the zinc-polymeric coating were not detected in the other exposure sites. The number of such fungi species was 19, 20 and 25 in the marine, rural-agrarian and industrial environments, respectively.

3. Mitosporic fungi belonging to *Cladosporium cladosporioides*, *C. herbarum*, *Alternaria alternata*, *Acremonium strictum*, *Paecilomyces parvus* are predominant and capable of developing on the zinc-polymeric coatings. Under certain environment conditions *Penicillium brevicompactum* (frequency of detection 14–63%), *Penicillium verrucosum* (22–26%), *Sporotrichum aurantiacum* (28%) can intensively develop on the zinc-polymeric coatings. In the rural-agrarian and industrial environments the following fungi were detected – *Arthrinium phaeospermum* (29 and 28%, respectively); *Candida albicans* (21 and 32%); *Oidiodendron echinulatum* (29 and 16%); *Paecilomyces parvus* (69 and 26%); *Penicillium chrysogenum* (19 and 27%); *Tilachlidium branchiatum* (29 and 13%); *Trichosporiella cerebriformis* (29 and 17%).

4. After 1.5 years of exposure the zinc-polymeric coatings exposed to the marine and rural-agrarian environments were deteriorated most markedly. The character of deterioration differed, the processes of fungi conidiogenesis were most clearly seen on the zinc-polymeric coatings exposed for 2 years to the industrial environment, where *Aspergillus fumigatus* developed most intensively, and to the marine environment, where *Cladosporium cladosporioides* developed. It testifies, that the zinc-polymeric coatings are not strong biocides and do not prevent the growth and formation of bioagents on their surface.

5. According to diffractograms all four zinc-polymeric coatings are sufficiently resistant to bioagents, although under the natural environment gradually lose their mass and the quantity of corroded zinc markedly changes, as well.

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