RESISTANCE TO THE ACTION OF FILAMENTOUS FUNGI UPON SOME COATINGS MATERIALS

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In order to determine the durability of polymer coatings using investigation techniques based on X-rays diffraction and combined techniques for thermal analysis (TG-DTA-DTG), one determined the changes of structure and their thermo-oxidative characteristics for 6 different types of paint having different characteristics, after subjecting them to UV radiation exposure (60W/m², between 300 and 400nm). The experimental results indicate that UV radiation induces various changes, depending on the type of paint, the paint topcoat films, the degree of crystallinity, its fragility and the exposure dose (the latter being between 0,0005 and 0,0150%/Wh/m²). Additionally, one determined the effects of the biological action of some microorganisms which in certain cases is initiated and may also be enhanced in the presence of UV radiation.

Keywords: painting materials, durability, thermal stability, UV resistance, diagnosis

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1. Introduction

In the complex buildings environments, the painting systems applied on steel, wood or concrete structures are exposed to a broad range of climatic factors (diurnal temperature variations, humidity, UV radiation), chemical factors (aggressive aerosols, industrial pollutants, acid rains), mechanical factors (wind carrying dust and sand particles, hail, mechanical deformations of the structure) and, as well, by an increased number of microbiological factors. The synergic action of the above-mentioned factors leads to the degradation of the coatings, requiring, most of the time, costly maintenance operation (materials, manpower, turn-off equipment) and have a negative impact upon the environment. In this context, an increased number of studies were made about the corrosion resistance and resistance to a broad range of stress factors with direct effect on some organic coatings, based on different polymers [1-4].

Modern painting materials are based on polymeric materials, mostly alkyls, epoxy or polyurethane based. [1, 2, 4 - 9]. Coatings are applied in liquid state and form a dry protecting solid film as a result to complex physical (solvent evaporation) and chemical processes. The most important chemical process is polymerization which is influenced by the content of the atmospheric oxygen, temperature, non-ionizing (UV, IR) and ionizing radiations.

Due to the fact that these polymers are voluminous molecules, it is difficult to be metabolized directly by microorganisms. Their metabolism is possible only after breaking-off the macro-molecules in smaller fractions, respectively, a polymerization degree n <200, which can pass through the cell membrane of the microorganisms [10].

Under these circumstances, the biodegradability of plastic materials is strongly influenced by the environment. The biodegradability is accelerated by solar or artificial light radiation, which breaks the C – C links, especially under the influence of UV radiation spectrum at $\lambda = 295$-400 nm, but also for visible spectrum $\lambda = 400$-700 nm. The heat and humidity appear to accelerate the metabolic processes, as they influence directly the biological film growth. Furthermore, the synergic action of the abiotic environment factors, accelerates the degradation of the polymers reducing substantially the degradation time.

However, one should mention here that there is a fine balance, an intensification of the UV radiation deteriorates the biological cells, due to its oxidative action of the microorganisms’ membranes, leading finally to their death [11]. The most active and efficient microorganism species which are involved in the natural biodegradation of the polymers are the filamentous fungi (such as: Aspergillus niger, Penicillium funiculosum etc.). Hyphae mycelium has the peculiar capacity of intruding between polymers macromolecules and breaking the C – C links, thus reducing significantly the polymerization degree [12]. On the
Resistance to the action of filamentous fungi upon some coating materials

other hand, heat, humidity and UV radiation accelerate the thermo-oxidative cracking process of the macromolecules, which makes it much easier biodegradable [13–17]. The microbial enzymes have a determinant role in biodegradation and biodeterioration of polymers [18], including painting materials, the most aggressive being those produced by the filamentous fungi [19–26]. One should notice that, after damaging of the protective coatings, the microorganisms have also a significant contribution to inducing and producing corrosion phenomena of the substrates [27–31], with a disastrous overall effect upon the integrity of the whole structure [19, 30, 31]. In this context, the issue of developing high performance protective coatings, biologically resistant, if possible, becomes of an utmost importance [7–9, 32].

Having in mind all these facts, the scope of this paper is to assess the resistance of some protective coatings versus the action of some filamentous fungi in the presence and in the absence of UV exposure.

2. Experiment

In order to assess the resistance to the action of the filamentous fungi, paint samples having a DFT (Dry Film Thickness) between 80 µm and 120 µm of materials S1 – S6 (Table 1) were subjected to a series of investigations.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Brand name</th>
<th>Producer</th>
<th>Resin type</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Sigmaprime 200 [33]</td>
<td>PPG</td>
<td>Epoxy</td>
<td>Primer</td>
</tr>
<tr>
<td>P2</td>
<td>Sigmacover 456 [34]</td>
<td>PPG</td>
<td>Modified epoxy</td>
<td>Topcoat</td>
</tr>
<tr>
<td>P3</td>
<td>Intergard 410 [35]</td>
<td>IP</td>
<td>Modified epoxy</td>
<td>Topcoat</td>
</tr>
<tr>
<td>P4</td>
<td>Hardtop [36]</td>
<td>JOTUN</td>
<td>Acrylic polyurethane</td>
<td>Topcoat</td>
</tr>
<tr>
<td>P5</td>
<td>Interthane 990 [37]</td>
<td>IP</td>
<td>Acrylic polyurethane</td>
<td>Topcoat</td>
</tr>
<tr>
<td>P6</td>
<td>Sigmadur 550H [38]</td>
<td>PPG</td>
<td>Polyurethane</td>
<td>Topcoat</td>
</tr>
</tbody>
</table>

The above presented commercial dye samples were not designed as special antifouling – antifungal paints, they are just standard products for industrial applications (ships, marine drilling platforms, bridges, wagons etc.). However, due to the fact that there is an increasing interest from the potential users to have more data regarding their particular resistance to various biological attacks, the purpose of the paper was to evaluate the mold resistance of materials investigated on unexposed and UV exposed interior and exterior surfaces, so that the industrial users will have some preliminary information to be able to select the proper dye in connection with the prevailing demands in any given application.
The applied paint samples were left for 7 days to make sure that the polymerization process was completed, and one carried out the assessment of resistance to fungal growth, on blank samples (protected from UV radiation) and exposed samples to UV radiation.

For the exposure to UV, at 60W/m², in the range of spectrum of \( \lambda = 300 - 400 \text{nm} \), one used a dedicated equipment allowing for a precise controlled UV exposure parameter - XENOTEST 440 (ATLAS – Material Testing Solutions).

The assessment of resistance to fungal growth was done using specific microbiological techniques [39], using a complete CZAPEK-DOX “B” culture medium (with sucrose – an easy metabolizing carbon source) and also on an incomplete CZAPEK-DOX “A” culture medium (without an easy metabolizing carbon source).

The CZAPEK-DOX “A” culture medium was prepared by dissolving in 1000 mL of deionised water of 2g of sodium nitrate (NaNO₃); 0,7g monopotassium phosphate (KH₂PO₄); 0,3g dipotassium phosphate (K₂HPO₄); 0,5g potassium chloride (KCl); 0,5g magnesium sulphate heptahydrate (MgSO₄·7H₂O); 0,01g iron (II) sulphate (FeSO₄); 30 g agar-agar. For the CZAPEK-DOX “B” culture medium, were added 30g of sucrose at 1000 mL of “A” culture medium.

The microbiological observations were done visually or with the aid of a stereomicroscope type OPTIKA SZM-2. The resistance to the fungus action was evaluated by giving marks, as per [40].

There were tested pure culture medium, inoculated with of Aspergillus niger spores and also mixed culture medium inoculated with culture of Stachybotris atra, Penicillium funiculosum, Cladosporium herbarum, Trichoderma viride, Paecilomyces variotii, Aspergillus flavus, Alternaria alternata, Aspergillus niger, Aspergillus ustus and Penicillium citrinum. The inoculation was done by spraying a solution containing \( 10^6 \) spores/ml.

The paint samples were laid on culture medium in Petri dishes of 60mm in diameter. After inoculation, the incubation took place in a climatic controlled chamber (incubator) MEMMERT UNB 400, at constant temperature of \( 30 \pm 20 \)°C and RH \( 80 \pm 10 \)% for 28 days.

2. The experimental results and their interpretation

Representative photos of the microbiological samples are shown in Fig. 1-7.
Fig. 1. Exposure of paint samples on CZAPEK-DOX „A” medium (P5 without UV exposure – pure culture medium of *Aspergillus niger* - 28 incubation days).

Fig. 2. Exposure of paint samples on CZAPEK-DOX „B” medium (P4 without UV exposure – pure culture of *Aspergillus niger* – 28 incubation days).

Fig. 3. Detail (X7) – P1 – without UV exposure, on “B” culture medium, pure culture of *Aspergillus niger* – 28 incubation days.

From Fig. 1 and Fig. 2, we may observe that on “B” culture medium, the growth of the mould is much more intense that in case of “A” culture medium due to the sucrose content of the “B” medium – easy to metabolize carbon source.

In Fig. 3, we find out that on the paint material P1, without UV exposure, on an area 1cm$^2$, during incubation, it developed only 7 fructifications (3 mature
having $0.05 < \Phi < 0.1\text{mm}$ and 4 young having $\Phi < 0.05\text{mm}$) on an undeveloped primary mycelium, visible only on microscope which indicates a good fungus resistance of the paint material.

By further analyzing Fig. 3, we observe that on P3 paint material, without UV exposure, after 28 days of incubation, has grown a consistent biofilm which covers approx. 30% of the sample’s area. Also, can be observed that, on the surface, has grown only mycelium and fructification of *Aspergillus niger* and *Trichoderma viride* which indicates a poor resistance of this paint type at the action of these fungi species.

![Detail image](image-url)
Fig. 5 shows that, on P4 paint material, without UV exposure, after 28 days of incubation, has grown a relatively consistent biofilm which covers approx. 20% of the sample’s area. Also, can be observed that, on the surface, has grown only mycelium and fructification of Aspergillus niger and Trichoderma viride which indicates a poor resistance of this paint type at the action of these fungi species.

Fig. 6. Detail (x7) – P5, exposed 20 hours at UV 60W/m², on “B” culture medium, mixed culture – 28 incubation days.
One may see in Fig. 6 that, on paint material P5, exposed to 60W/m$^2$ UV radiation for 20 hours, after 28 incubation days, has grown a relatively consistent biofilm which covers about 55% of the sample area. It also can be observed that on the sample surface has grown only mycelium and fructification of *Aspergillus niger* and *Trichoderma viride* which indicates a poor resistance of this paint type at the action of these fungi species.

Fig. 7 shows that, on paint material P6, exposed to 60W/m$^2$ UV radiation for 92 hours, after 28 incubation days, has grown, around the sample, fructifications of long *conidiophores* (slanted over the paint samples area) having a primary mycelium in the culture medium. On samples area it can be observed – only at microscope – few undeveloped primary mycelium having few small and undeveloped fructifications.

Microbiological monitoring during and after the incubation period shows that on culture media inoculated with mixed cultures have developed only *Aspergillus niger* and *Trichoderma viride*, which indicates that these two species
Resists to the action of filamentous fungi upon some coatings materials presents a maximum capacity of biodeterioration of the investigated samples which is in line with results reported in [13, 30, 31, 41] for different types of polyethylene.

The assessment of the percentage of mould growth on samples’ surface (done with the aid of the microscope software for image processing and based on the ratio of the colour shades) and the score (marks from 0 to 5) [34] are synthetically shown by Table 2.

Table 2

<table>
<thead>
<tr>
<th>Paint sample</th>
<th>Melds growth, in media:</th>
<th>Assessment</th>
<th>Assessment</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>coverage degree [%]</td>
<td>“A”</td>
<td>“B”</td>
<td>“A”</td>
</tr>
<tr>
<td>P1 W&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>0 0.1 0.2 0.3 0.4 0.5</td>
<td>1 1 1 1 1 1</td>
<td>0 0 0 0 0 0</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>P2 W&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>0 0.1 0.2 0.3 0.4 0.5</td>
<td>1 1 1 1 1 1</td>
<td>0 0 0 0 0 0</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>P3 W&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>0.3 0.4 0.5 1 2</td>
<td>0 0 0 0 0</td>
<td>0 0 0 0 0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>P4 W&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>0 0.1 0.2 0.3 0.4 0.5</td>
<td>1 1 1 1 1 1</td>
<td>0 0 0 0 0 0</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>P5 W&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>0 0.1 0.2 0.3 0.4 0.5</td>
<td>1 1 1 1 1 1</td>
<td>0 0 0 0 0 0</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>P6 W&lt;sub&gt;UV&lt;/sub&gt;</td>
<td>0 0.1 0.2 0.3 0.4 0.5</td>
<td>1 1 1 1 1 1</td>
<td>0 0 0 0 0 0</td>
<td>0 0 0 0 0 0</td>
</tr>
</tbody>
</table>

Notations: P1 ÷ P6 – in accordance with Table 1; W<sub>UV</sub> – without UV expose; UV<sub>1</sub> – exposed 92 hours to 60W/m<sup>2</sup> UV radiation (at 30°C and RH=50%); UV<sub>2</sub> – exposed 20 hours to 60W/m<sup>2</sup> UV radiation (at 30°C and RH=50%); WMG - without melds growth; “A” - CZAPEK-DOX media without sucrose; “B” - CZAPEK-DOX media with 30g/l sucrose; An – pure culture of Aspergillus niger; MC – mixed culture.

*Assessment – in accordance with [34]: 0 = without microbiological colonies; 1 = colonies visible only at the microscope; 2 = colonies visible with the naked eye, up to 25% of the area; 3 = colonies visible with the naked eye, unto 26÷50% of the area; 4 = colonies visible with the naked eye, unto 51÷75% of the area; 5 = colonies visible with the naked eye, over 75% of the area.

The analysis of data presented in Table 2 shows that the resistance to the action of the melds of the tested samples significantly decreases – 1 up to 2 score marks, function of each type of paint, further to the UV exposure. This can be explained by the fact that UV action initiates cross-linkings, followed by the thermo-oxidation processes, which lead to cracking of the paint material molecules.

The process of UV degradation of paint samples P1 ÷ P6 was highlighted by thermo analysis (TG-DTG-DTA) and X-ray diffraction analysis (XRD) [42].
By comparing the variation of the crystallinity of the paint samples which were exposed to UV, as reported in [42] (Table 3), can be observed that there is a direct correlation between resistance to the action of melds and the specific variation of the crystallinity degree \([\% / \text{Wh/m}^2]\), respectively a growth of the specific variation of the crystallinity degree \([\% / \text{Wh/m}^2]\) is correlated with a decrease of the resistance to the action of filamentous fungi (especially to *Aspergillus niger* and *Trichoderma viride*) of the investigated paint samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial [%]</th>
<th>Final [%]</th>
<th>UV exposure (60W/m²) [hours]</th>
<th>Specific variation [%/Wh/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>73.9</td>
<td>69.2</td>
<td>92</td>
<td>-0.0009</td>
</tr>
<tr>
<td>P2</td>
<td>59.2</td>
<td>62.1</td>
<td>92</td>
<td>0.0005</td>
</tr>
<tr>
<td>P3</td>
<td>64.6</td>
<td>82.7</td>
<td>20</td>
<td>0.0151</td>
</tr>
<tr>
<td>P4</td>
<td>58.9</td>
<td>64.8</td>
<td>20</td>
<td>0.0049</td>
</tr>
<tr>
<td>P5</td>
<td>58.7</td>
<td>59.4</td>
<td>20</td>
<td>0.0006</td>
</tr>
<tr>
<td>P6</td>
<td>52.8</td>
<td>55.3</td>
<td>92</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

This can be explained by the fact that UV action initiates cross-linking, followed by the thermo-oxidation processes, which lead to cracking of the paint material molecules. Similar findings are also reported in discussed in [42].

Further to the analyse of data given in Table 2, the investigated paint samples can be ordered as a function of their resistance to the action of the filamentous fungi, as follows: \(P1 > P2 = P6 > P4 = P5 > P3\).

### 4. Conclusions

By using specific microbiology techniques, one assessed the resistance to the action of the filamentous fungi of 6 different freshly applied types of paint which were also subjected to an accelerated ageing by UV exposure 60W/m². As a result of the analysis of the experimental data and of the microbiological observations, it was found out that:

- The resistance to the action of moulds of the paint materials which were subjected to an accelerated ageing by UV exposure is significantly lower – 1 to 2 score marks, as a function of the type of paint – than in case of the blank samples, which were not exposed to UV;

- The resistance to the action of moulds of the tested samples decreases when their crystallinity degree increases further to UV exposure such as that the paint sample having the minimum specific variation of the crystallinity (– 0.0009%/Wh/m²) further to UV exposure exhibits the best resistance to the action of moulds (P1) and, vice versa, the paint sample P3, which has a maxim specific
variation of the crystallinity (0.0151 %/Wh/m$^2$) exhibits the minimum resistance to the action of moulds;

- On the culture medium inoculated with mixed culture spores were identified only growths of *Aspergillus niger* and *Trichoderma viride*;
- Systematically, the resistance to the action of the mixed culture medium is lower than resistance to the action of pure *Aspergillus niger* culture medium.

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