INACTIVATION OF *ASPERGILLUS NIGER* ON PAINTS CONTAINING ZnO

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Abstract

Many paints contain special additives such as biocides which act as a prevention against biodeterioration. Presence of nanoparticles of silver and copper may inhibit the grow of microorganism. Self cleaning facade paints containing photocatalytic particles (mostly TiO_2) appear also on the market. Such paints are after irradiation of sunlight no to susceptible to soiling and thus help to keep exterior of building clean. Another type of paints is prepared with aim to improve air quality in exterior via photocatalytic oxidation organics compounds such as acetaldehyde, formaldehyde etc. This contribution deals with the application of ZnO particles to water based acrylic paints. The objective is to determined antifungal capability against A. niger. Attention will be also paid to determination of photocatalytic activity. Photocatalytic activity will be determined using indicator ink containing Resazurin dye. This method is based on observation of color change from pink to blue which occurs on photocatalytic surface.

Keywords: Self-cleaning, ZnO, *Aspergillus niger*, photocatalysis

1. INTRODUCTION

Self-cleaning paints contains besides usual pigment and fillers also particles of photocatalytic materials mostly TiO_2 of anatase modification but also paints containing ZnO [1] are not unusual. Such surfaces are after irradiation by UV light not to susceptible to soiling [2] and also exhibit superhydrophilic properties, which means that water do not formed droplets but it flows out from the surface in the form of thin film due to the decrease of water contact angle [3]. Such paints are also potential application to prevent biodeterioration of buildings material [4].

The resistance of building materials to micro-organisms is one of their monitored properties [5]. It is used to be tested the resistance to bacteria, mould and fungi. This paper deals with the resistance of the paint containing ZnO to fungi.The deal of this contribution is preparation and characterization of laboratory paints containing ZnO in term its photocatalytic and antifungal properties using *Aspergillus niger.*

2. EXPERIMENTAL

As a photocatalyst was used commercial ZnO with crystall size about 66 ± 3 nm (Sheerrer equation) and specific area 6 m^2/g (BET isotherm). Applying of ZnO in aqueous acrylic dispersion with non-photoactive rutile pigment, calcium carbonate and special additives were prepared samples of interior paints containing 8 % ZnO (in dry matter) Beside photoactive paint also reference paint without photocatalytic pigment containing only inactive rutile was prepared. Samples of paints were coated on glass (5x10 cm) using wire wound rot, the thickness of wet film was 120µm.

Photocatalytic activity was measured by method published in [6] which is based on reduction of Resazurin ink. Samples with photoactive coating were covered by Resazurin ink using 24 micron K bar, after drying samples were periodically irradiated by UV A light (λ = 351 nm, intensity 2 mW/cm^2). During UV exposition, it comes to reduction of Resazurin (blue) to Resorufin which is pink. Photocatalytic activity is than expressed as time of UV exposition which is needed to reach 90 % of overall color change.

Antifungal properties were studied using inactivation of *Aspergillus niger* [7]. Petri dishes with malt extract agar (Oxoid, Great Britain) containing samples of paints (25 x 25 mm) were inoculated by spraying of suspension of physiological solution containing spores of *Aspergillus niger* (Czech Collection of Microorganisms). Reference plates without paint samples were used as a control of growth of *Aspergillus niger*. Each test was performed with samples in five replicates. Samples were cultivated at temperature 23 ± 3 °C in light/dark cycle (16/8 hours). The experiment was evaluated as antifungal activity of tested paint visually after 28 days. The growth and development of mould mycelium on the dish and surface of the coating on a glass mat was monitored during the time of experiment to obtain comparison for paint with and without additive of 8 % ZnO. The scale used to evaluate mold growth is based on the standard ČSN EN ISO 846 (0 - no growth, 1 - growth visible only under the microscope, 2 - growth visible to the naked eye, covering less than 25 % of the surface, 3 - growth visible to the naked eye, covering less than 50 % of the surface, 4 - significant growth covering more than 50 %, 5 - surface covered with 100 %).

3. RESULTS AND DISCUSION

In **Figure 1**, there is illustrated dependence of red channel depending on time of UV irradiation for 6 paints samples containing 8 % of ZnO (in dry matter). We can see that during UV irradiation it comes to increase of Red channel, which corresponds to gradual color change of blue Resazurin to pink Resorufin. After 85 seconds of irradiation we can see in dependence in **Figure 1** typical elbow which corresponds to the time when the color of ink stop changing. With further UV irradiation the values of red channel didn't change and Photocatalytic activity is than expressed as time which is needed to reach 90 % of overall color change (time to bleach - Ttb_{90}). Calculated values are calculated by red squares and corresponds to the 83 ± 3 s. Reference paint without photocatalytic ZnO do not who measurable photocatalytic activity as results from **Table1**.

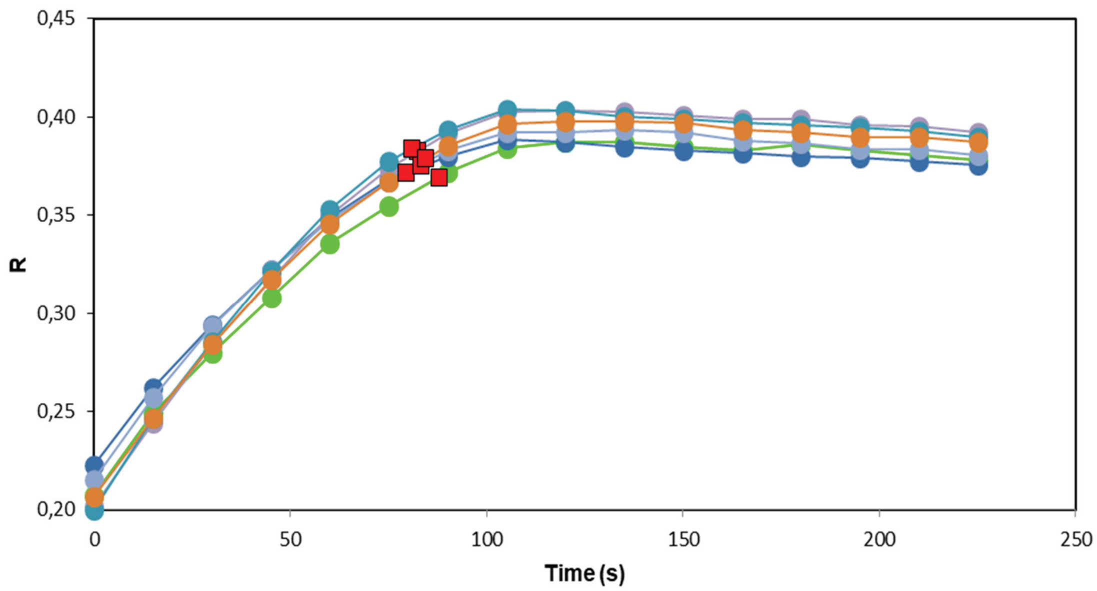


Figure 1 Dependence of photocatalytic experiment - paint containing 8 % of ZnO (experiment was proved for 6 identical samples, calculated TTb_{90} values express as red full squares)

Similar results of photocatalytic activity using Resazurin ink was observed in paper [8] in which photocatalytic activity of water based acrylic paint containing 8 % of TiO_2 was studied. On the other hand in paper published by Hochmanová et al. [1] was observed higher activity for ZnO compared to TiO_2 (measured using degradation of azo dye AO7).

Table 1 Comparison of color change of Resazurin ink on paint containing 8 % of ZnO (up) and reference sample

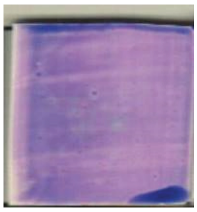
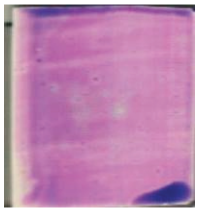
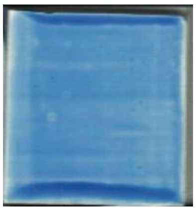
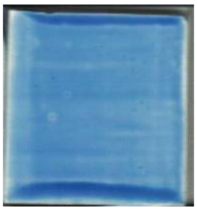
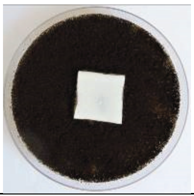
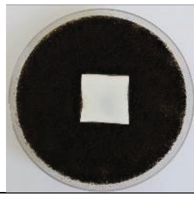
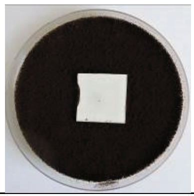
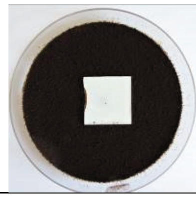
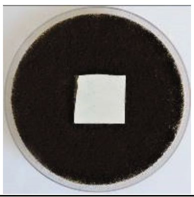
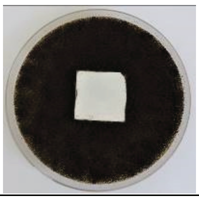
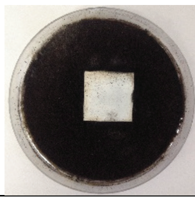
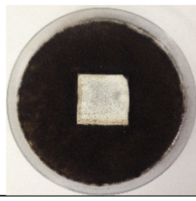
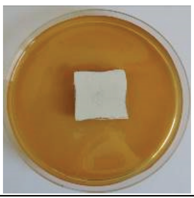
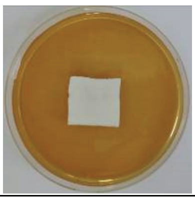
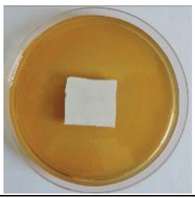
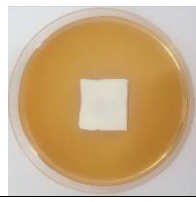
Sample/Time of UV exposition (seconds)	**0**	**15**	**30**	**60**
Active paint 8 % of ZnO				
Reference paint without ZnO				

Table 2 *Aspergillus niger* growth on the surface of paint samples during experiment

Sample/day of cultivation	**6th**	**8th**	**12th**	**28th**
Active paint 8 % of ZnO				
Reference paint without ZnO				
Reference paint without ZnO without inoculation				
Control				

Aspergillus niger growth was monitored and noted for one month. The growth of mold is presented in the photos taken during experiment in **Table 2**. In **Table 3** there are shown results of the selected time intervals as an average value obtained from five repetition of samples. The results did not show significant difference between tested paint during the first six days. At eighth day first variation in mold growth was observed by kind of paint samples with inoculation. Growth of Aspergillus niger was more massive in the case of a sample without the addition of ZnO. It should be noted that even on the sample with the addition was the growth observed (growth visible only under the microscope - **Table 3**). Growth was registered up to the 28th day after inoculation. Even after the basic monitoring (28 days) has not acquired growth tendencies such as the sample without the addition of ZnO (meaning 50 days after inoculation). Those results are in the good agreement with paper [9] mentioned antifungal properties of ZnO.

Table 3 Evaluation of mold growth on the surface of paint samples

Sample/day of cultivation	**6th**	**8th**	**12th**	**28th**
Active paint 8 % of ZnO	0	0	0	1
Reference paint without ZnO	0	1	2	3
Active paint 8 % of ZnO without inoculation	0	0	0	0
Reference paint without ZnO without inoculation	0	0	0	0
Control	4	5	5	5

4. CONCLUSION

Photocatalytic and antifungal activity of water based acrylic paints containing 8 % of ZnO was determined. Prepared paints exhibit measurable photocatalytic activity which was quantified as Ttb_{90} (83 ± 3 s). Obtained results were similar to Ttb_{90} values determined for paints containing TiO_2. Antifungal properties was proved using *Aspergillus niger* as a model organism. After 8 days of the test apparent difference of mold grow was recorded. In sample containing ZnO, the growth of model organism was much lower which indicate antifungal properties of ZnO under presented setup of experiment. Given the obtained results it can be classified that the prepared coating has antifungal effect.

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