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INFLUENCE OF SHELF-LIFE STABILITY ON ANTIMICROBIAL EFFICIENCY OF AQUEOUS ACRYLIC DISPERSION CONTAINING NANO OXIDES AND ORGANIC BIOCIDE

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Antimicrobial paints were formulated based on various nano particles of zinc oxide and organic biocide. The aqueous acrylic dispersion was used as a binder for this system. A control paint without nanoparticles was formulated. The antimicrobial ability, shelf-life stability and photoactivity were assumed in these paints based on nano zinc oxide with organic biocide. It is possible to observe the photoactivity thanks to a change in organic dyes due to oxidative-reductive reaction. The agar dilution method was used for a test of the antimicrobial ability. The Escherichia coli, Pseudomonas aeruginosa and Staphylococcus aureus were chosen as test bacteria. A great antibacterial inhibition of Escherichia coli and Staphylococcus aureus sis exhibited both coatings, and they are antimicrobially active after 12 months of shelf stability.

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Introduction

The world-wide spread of diseases is a great problem of the modern society [1]. Infection is a major medical complication associated with health care environments [2]. Infection control is of utmost importance in various places, which require a high level of hygiene as technical applications for antimicrobial coatings include medical products, packaging materials or filters used in air-conditioning systems. Hospitals, pharmaceutical production units, food factories, *etc*. need to be rigorously disinfected in order to destroy pathogenic microbes [3-5].

Waterborne coating systems are complex mixtures of polymers, pigments, fillers and functional additives. The additives are used to improve different appearance or performance characteristics of the final coating. Very important is also shelf-life stability because of long term efficiency of the paint. Unexpected synergies or undermining of performance may arise when certain components are included. The performance additives can be broadly grouped into three major types based on which characteristic is being modified:

- chemical – antioxidants, UV absorbers, thermal stabilizers;
- physical – flow aids, rheology modifiers, de-foamers, dispersants;
- biological – antimicrobials, antifungals, algaecides.

The ability of all of these additives to fulfill their roles is greatly impacted by the environment in which they operate. Antimicrobials are one class of additive that is very dependent on what else is in the system formulation [6].

Zinc is biogenic and because of it is necessary for the cells in a small amount but it is toxic in a high amount. It is necessary to control its amount [7].

The photocatalytic process of ZnO involves the generation of electron-hole pairs when it is exposed to light. The holes are able to react with nearby molecules to produce oxidants. The reaction of zinc oxide with water produces the hydroxyl radical (OH^-). In the case of oxygen, the result is the superoxide molecule (O_2^-). Zinc oxide and other semiconductor materials may provide unusual electronic and chemical mechanisms for inhibiting the growth of microorganisms in similar way as titanium dioxide [8,9]. These radicals eventually attack bacteria or viruses in terms of inhibiting DNA clonal processing, destroy coenzymes, enzymes in the self-regeneration and enzymes in the respiratory system. As a result, the radical stops the reproduction of bacteria and molds, thereby inhibiting bacteria growth or preventing virus DNA multiplication [10-12].

Experimental

The paints used were based on an acrylic pigment dispersion and additives. The concentration of the antimicrobial additive was 1.4 wt. %. The antimicrobial ability, stability, and photoactivity were determined for two paints with different ZnO nanoparticles, i.e., 35 and 60 nm. The organic biocide used was based on Thiabendazole and *N*-Octylisothiazolinone. The paint without additives was used as a test one.

The photoactivity is dependent on air humidity and ultra violet (UV) radiation. It is possible to observe the photoactivity thanks to a change in organic dyes due to oxidative-reductive reaction. Degradation of Orange II is measurable thanks to a change in colour of the solution. A spectroscopic method was used for this measurement (485 nm). The absorbance of solution on paint was measured before and after UV irradiation and also before and after exposure to visible light.

The test of the antimicrobial efficiency was made on these paints, too. The microbial cultures from Collection of University of Pardubice were used. The *Escherichia coli, Pseudomonas aeruginosa* and *Staphylococcus aureus* were chosen as test bacteria.

Testing of bacteria was made as follows. The paints were coated on filter paper (5×5 cm). Instruments and tested films were sterilized, test bacteria were pre-incubated on sterilized Petri dish with an MPA agar for 24 hours at 37 °C and then the test inoculum with the density of 10^6 bacteria ml^{-1} of each bacteria was prepared. Each tested film was put onto agar in a sterilized Petri dish and a test inoculum was put onto a surface and spread on the whole space of agar. The Petri dishes were incubated for 24 hours at the temperature of 37 °C, and then the number of colonies was counted. The inoculation of bacteria onto specimen is shown in Fig. 1.

The antibacterial efficiency was tested according to way mentioned here in three different times. The coatings were painted on sterilized filter paper immediately after preparation and divided into two parts. One part was tested im-

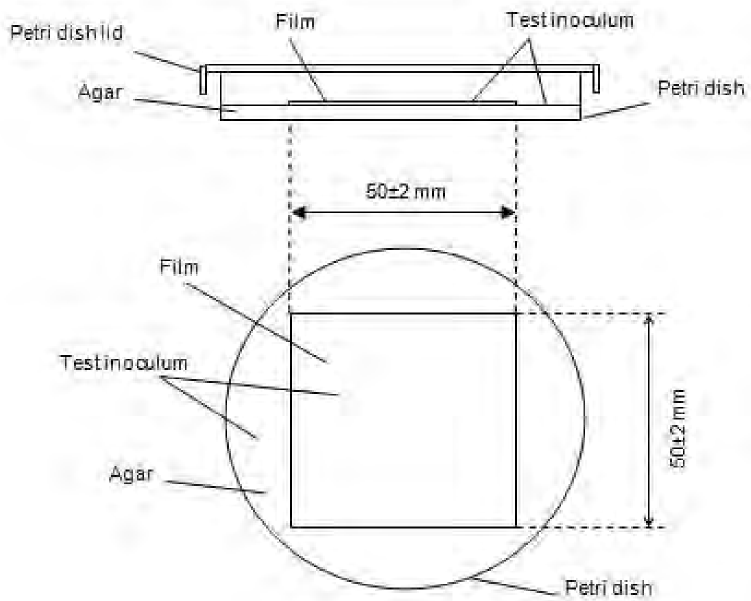

Fig. 1 Inoculation of bacteria onto specimen in the Petri dish

mediately after the preparation and the other was left for 12 months in a paper box and after that the samples were tested. The other part of samples was painted after 12 months in a can, and then the antibacterial test was done.

Results and Discussion

The photocatalytic activity was measured for the coatings containing additives with different size of nano ZnO and aqueous dispersion based on thiabendazole (TBZ) and *N*-octylisothiazolinone (N-OIT) and a coating without additives after exposure to UV radiation and visible light. The change in absorbance of Orange II was observed and the results are shown in Figs 2 and 3. The coatings containing both nano ZnO types exhibit photocatalytic activity when they are exposed to UV radiation and visible light.

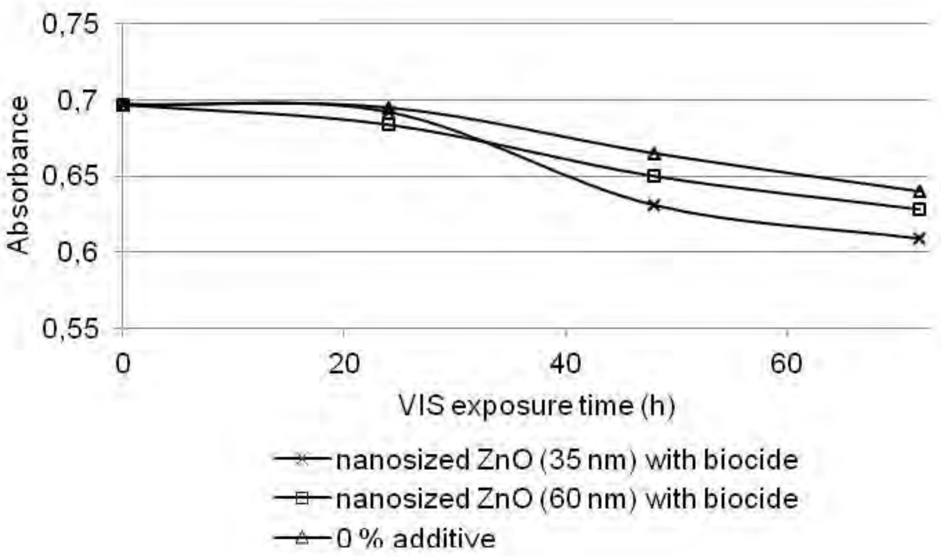

Fig. 2 Change of absorbance of Orange II after exposure to visible light on films

The antibacterial efficiency of coatings containing combination of nano ZnO (35 nm or 60 nm) with aqueous dispersion based on Thiabendazole (TBZ) and *N*-octylisothiazolinone (N-OIT) and coating without pigment is shown in Figs 4-6. It is obvious that the coatings show very good results against two of the bacteria (*Escherichia coli* and *Staphylococcus aureus*) compared to the coating without additives. Antimicrobial efficiency was pure against *Pseudomonas aeru ginosa* for both of samples. Antibacterial efficiency is high against *Escherichia coli* and *Staphylococcus aureus* after 12 months of shelf stability too. The antibacterial efficiency was tested according to the way mentioned in Experimental in three different time periods.

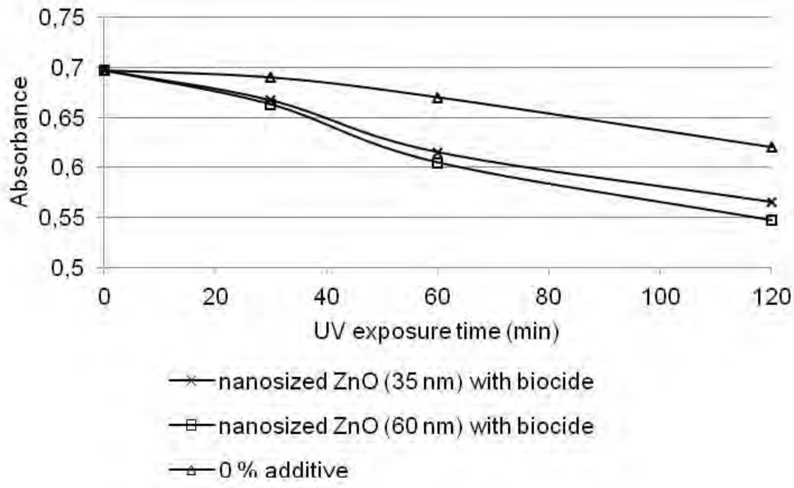

Fig. 3 Change in absorbance of Orange II after exposure to UV radiation on films

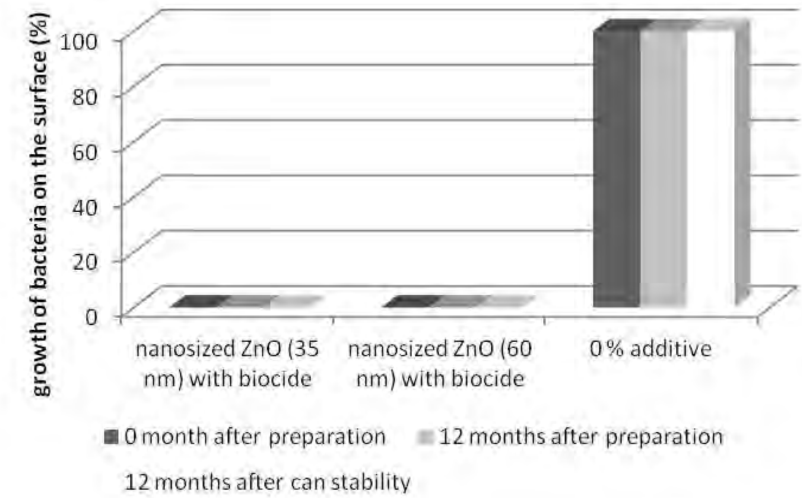

Fig. 4 Antibacterial efficiency against *Escherichia coli* of coatings containing nano ZnO in different size with biocide and coating without additives

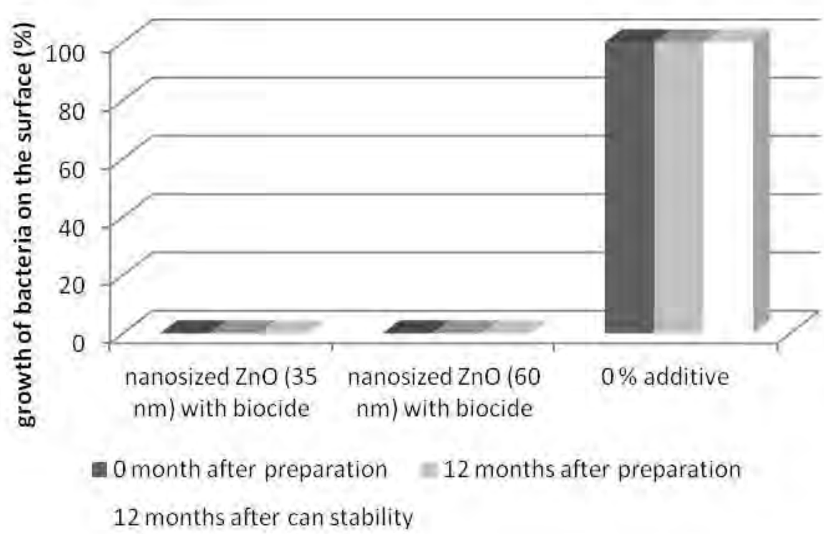

Fig. 5 The antibacterial efficiency against *Staphylococcus aureus* of coatings containing nano ZnO in different size with biocide and coating without additives

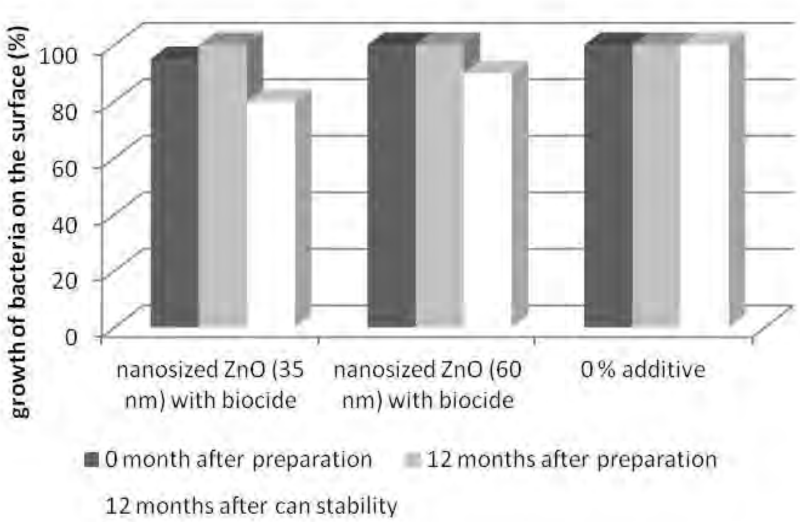

Fig. 6 Antibacterial efficiency against *Pseudomonas aeruginosa* of coatings containing nano ZnO in different size with biocide and coating without additives

Conclusion

The tested samples showed a high antimicrobial efficiency for both of chosen particle sizes of the pigment against *Escherichia coli* and *Staphylococcus aureus*. A combination of nano ZnO with aqueous dispersion based on thiabendazole (TBZ) and *N*-octylisothiazolinone (N-OIT) was not sufficient to inhibit *Pseudomonas aeruginosa*. The shelf stability was high for *Escherichia coli* and *Staphylococcus aureus* after 12 months too. These paints seem to be a very good alternative for the antimicrobial coating.

Acknowledgement

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