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THE INFLUENCE OF BENTONITES MODIFIED WITH QUATERNARY AMMONIUM SALTS ON BIOCIDAL PROPERTIES OF COMPOSITIONS OF WATER-DILUTABLE PAINTS AND LACQUERS, AND MINERAL PLASTERS

*The research led to the obtainment of compositions of water-dilutable paints and lacquers as well as mineral plaster with the additive of nanofiller called Nanobent[®] (bentonite modified with quaternary ammonium salt) which is a commercial product of ZGM Zębiec near Starachowice. The resistance of the above-mentioned substances to mould fungi *Aspergillus niger* and *Penicillium chrysogenum* was tested. The best results were obtained for the composition with 3% additive of Nanobent ZR2 filler which practically completely inhibited the growth of mould fungi, even in the presence of whole culture medium containing glucose.*

Keywords: acrylic emulsion paint, acrylic lacquer, mineral plaster, bentonite, quaternary ammonium salt, Nanobent ZR and ZR2, *Aspergillus niger*, *Penicillium chrysogenum*, fungicidal properties

Introduction

Paints, lacquers, mineral plasters and other water-dilutable products are exposed to the attack of bacteria, yeast, and fungi. An environment of high humidity is perfect for growth of those microorganisms. Fungi grow well in conditions of lower humidity and usually attack the surface of a coating, which phenomenon was described by [Spychaj, Spychaj 1996]. Coating-making materials containing proteins (lecithin, casein or polysaccharides) often used as condensing

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agents described in the German patent [1990] are especially susceptible to microorganism attack. Those compositions can be protected by additive of biocidal agents – bactericides and fungicides. Bactericides are preservatives which prevent undesired changes in liquid paints, and fungicides deter destruction of dry coating by microorganisms from fungi group. Bacteria may penetrate into paints during production, filling up and emptying of containers, and during transport or storage, which was described by [Edge M. et al. 2001; D’Arcy 2001].

Gobbert et al. [2002] observed that in order not only to counteract microorganism action in finished product but also to protect coating made of that product, biological contamination that may occur in technological process should be eliminated.

The aim of this research was enrich the compositions of emulsion paint, acrylic lacquer and mineral plaster with bentonite modified with quaternary ammonium salt of multi-functional action, i.e. simultaneously acting as a tixotropic agent, condensing agent and fungicidal agent.

Experimental part

Testing of the resistance to microorganisms of the compositions of emulsion paint, acrylic lacquer and mineral plaster with an additive of modified bentonites were carried out in accordance with methodology described in line with recommendations of Polish standard PN-EN ISO 846.

The following materials were used in the tests:

1. Salt-agar culture medium without glucose,
2. Salt-agar culture medium with glucose added,
3. Solution of mineral salts,
4. Mould fungus *Aspergillus Niger ATCC 16404*,
5. Mould fungus *Penicillium chrysogenum ATCC 10106*,
(materials 1–5 are produced by MERCK Company, Germany)
6. Emulsion paint,
7. Acrylic lacquer,
8. Mineral plaster,
(materials 6–8 are produced by “Śnieżka” Company, seated in Pustynia near Dębica, they are “raw” products without any tixotropic and biocidal agents added)
9. Nanofiller Nanobent[®] ZR1,
10. Nanofiller Nanobent[®] ZR2,
(materials 9–10 are produced by ZGM “Zębiec” Company in Zębiec near Starachowice)
11. Finishing plaster by “Nowa Doliny Nidy” Company, Pińczów.

The test consisted in exposure of the compositions of emulsion paint, acrylic lacquer and mineral plasters with the additive of Nanobent (bentonite modified with quaternary ammonium salt) to mould fungi. The samples were applied on gypsum discs and exposed to the suspension of mixture of fungal spores in the presence of whole or deficient culture medium and incubated for a defined time in specified conditions of temperature and humidity. Each inhibition of growth on the gypsum disc as well as on the culture medium indicates fungicidal action of the coating-making substance additive. After the exposure of a sample finished, the sample was assessed visually in accordance with the scale given in table 1.

In order to test the resistance of the compositions of paints, water-dilutable lacquers and mineral plasters to mould fungi, previously prepared gypsum discs of the diameter of 3 cm and the thickness of 2–3 mm were used. To obtain an impenetrable surface the discs were twice covered with the adequate tested composition with one-day interval.

Two groups of samples were prepared:

- group 0: control samples inoculated with microorganisms without modified bentonite added,
- group I: samples inoculated with microorganisms and incubated with the additive of modified bentonite.

At least five samples from each composition were prepared for visual assessment.

Previously prepared gypsum disc was placed on a sterile Petri dish and the dish was then filled with culture medium up to the height of about 5 mm. 5 ml of a solution of mineral salt and wetting agent was added to each sample with culture. The surface of spores' culture was gently scraped off with a sterile inoculating loop in order to obtain the water suspension of spores. The operation was repeated three times with the same test tube. Then the suspension of spores of each culture was mixed with a glass rod and filtered through a thin layer of sterile cotton wool in order to remove fragments of mycelium. Two sterile Petri dishes were filled with culture medium and inoculated with one drop taken from each suspension of spores. Incubation was carried out in the temperature of $24^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in an incubator for 3–4 days.

Using a Pasteur pipette a drop of the spores' suspension was evenly applied on the surface of each sample from group I and on agar. The samples were incubated for 4 weeks in an incubator in the temperature of $29^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and humidity of 95%. If the mycelium growth was visible to the naked eye during the 4-week incubation period, the test was finished. If the result was not positive, the time of the test was extended.

Table 1. The results of the tests of the resistance of the compositions of emulsion paint, acrylic lacquer and mineral plaster to the action of mould fungi *P. chrysogenum* and *A. niger* after 28 days of incubation (Grades: 0–1 very good result, 2–4 some infected areas occurred, 5–6 negative result)

*Tabela 1. Wyniki badań odporności kompozycji farby emulsyjnej, lakieru akrylowego, tynku mineralnego na działanie grzybów pleśniowych *P. chrysogenum* i *A. niger* po 28 dniach inkubacji (Oceny: 0–1 bardzo dobry wynik, 2–4 – istnieją obszary zakażone, 5–6- negatywny wynik)*

No. Lp.	Type of coating used <i>Rodzaj zastosowanej powłoki</i>	Fungi growth assessment <i>Ocena wzrostu grzybów</i>			
		On individual samples <i>Na poszczególnych próbkach</i>	min	max	Average of 6 samples <i>Średnia z 6 prób</i>
1	Gypsum <i>Gips</i>	6,6,6,6,6,6	6	6	6
With the additive of glucose <i>Z dodatkiem glukozy</i>					
2	Paint without additives <i>Farba bez dodatków</i>	6,6,6,6,6,6	6	6	6
3	Paint with 3% Nanobent ZR2 <i>Farba z 3% Nanobent ZR2</i>	3,3,3,2,2,2	2	3	2.5
4	Lacquer without additives <i>Lakier bez dodatków</i>	6,6,6,6,6,6	6	6	6
5	Lacquer with 3% Nanobent ZR2 <i>Lakier z 3% Nanobent ZR2</i>	3,3,2,2,2,2	2	3	2.3
6	Plaster without additives <i>Tynk bez dodatków</i>	6,6,6,6,6,6	6	6	6
7	Plaster with 3% Nanobent ZR2 <i>Tynk z 3% Nanobent ZR2</i>	3,3,2,2,2,2	2	3	2.3
Without the additive of glucose <i>Bez dodatku glukozy</i>					
8	Paint without additives <i>Farba bez dodatków</i>	2,2,1,1,1,1	1	2	1.3
9	Paint with 3% Nanobent ZR2 <i>Farba z 3% Nanobent ZR2</i>	1,1,1,0/1,0/1,	0	1	0.75
10	Lacquer without additives <i>Lakier bez dodatków</i>	0/1,1,1,1,1,1	0	1	0.83
11	Lacquer with 3% Nanobent ZR2 <i>Lakier z 3% Nanobent ZR2</i>	0/1,0/1,0/1,0/1,0/1,0/1	0	0	0
12	Plaster without additives <i>Tynk bez dodatków</i>	6,6,6,6,6,6,6	6	6	6
13	Plaster with 3% Nanobent ZR2 <i>Tynk z 3% Nanobent ZR2</i>	1,1,1,1,1,1,1	1	1	1

In the first place the growth of mould fungi was assessed with the naked eye, and then, if there was such need, it was verified under the microscope (magnification of 40×). The record of visual assessment results contains photographic

documentation. If the results of visual assessment of the samples in one group differed by more than two scale intervals, the determinations were repeated using new samples.

Analysis and discussion of results

In the first stage of research the resistance of emulsion paint, acrylic lacquer and mineral plaster without any nanofillers added to mould fungi *Aspergillus niger* and *Penicillium chrysogenum* was tested. Then tests of the compositions with the additive of Nanobent ZR1 filler were conducted. The resistance of a substratum (gypsum discs) to mould fungi was tested as well. The time of fungi incubation on the tested samples was 28 days on deficient salt-agar culture medium without glucose and on whole culture medium with glucose added. The obtained test results are presented in photo 1–7.

As it can be seen in photo 1 (attached) the whole surface of the gypsum disc was covered by mould fungus *Aspergillus niger*. In those conditions the gypsum disc proved to have been a perfect material for fast and effective growth of the mould fungus. It should be mentioned here, that gypsum absorbs and accumulates humidity well, which results in good comparability of fungi growth in laboratory conditions with the conditions present in practice, which was one of the reasons why we have decided to use gypsum disc as a substratum. Subsequently tests of resistance of the composition of emulsion paint without any additive of filler (so-called control sample – comparative sample) to mould fungus *Aspergillus niger* were carried out. As it could have been expected, the lack of fungicidal additives in the emulsion paint contributed to fast growth of the mould fungus. The whole surface of the gypsum disc with the layer of applied paint was covered by the fungus (photo 1).

The following stage of the tests allowed determination whether introduction of Nanobent ZR1 into the tested compositions effectively inhibited the growth of mould fungi. The nanofillers were added to the compositions of emulsion paint, acrylic lacquer and mineral plaster in the amounts of 1.5% or 3% of the weights. Photo 2a presents a gypsum disc with emulsion paint containing filler applied on it. The disc was exposed to mould fungus *Aspergillus niger*. As it can be seen that disc was covered by the mould fungus in 90%, which might have been a result of either penetrable surface of the coating or weak biocidal properties of the modified bentonite used, and also of conditions created by whole culture medium which were favourable to the growth of the mould fungus. In photo 2b, which illustrates the result of incubation for the composition in which the content of Nanobent ZR1 additive was 3%, it was observed that the addition of the above-mentioned bentonite had a clear influence on the improvement of biocidal properties. Around 40% of the disc surface was not infected by the mould fungus.

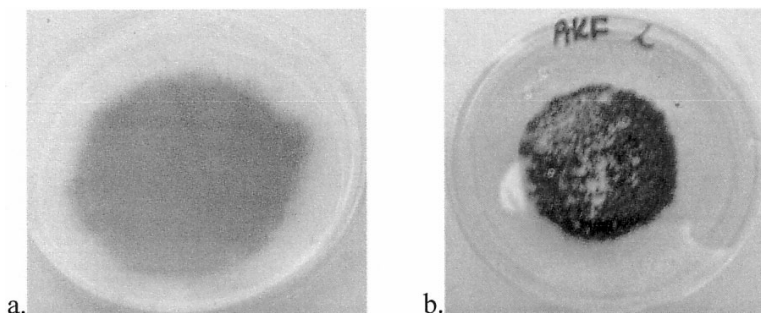


Photo 1. The appearance of: a – gypsum disc, b – emulsion paint without any Nanobent added exposed to mould fungus *Aspergillus niger* on whole culture medium

*Fot. 1. Wygląd: a – krążka gipsowego, b – farby emulsyjnej bez dodatku Nanobentu, w wyniku działania grzyba pleśniowego *Aspergillus niger* na pożywcę pełnowartościowej*

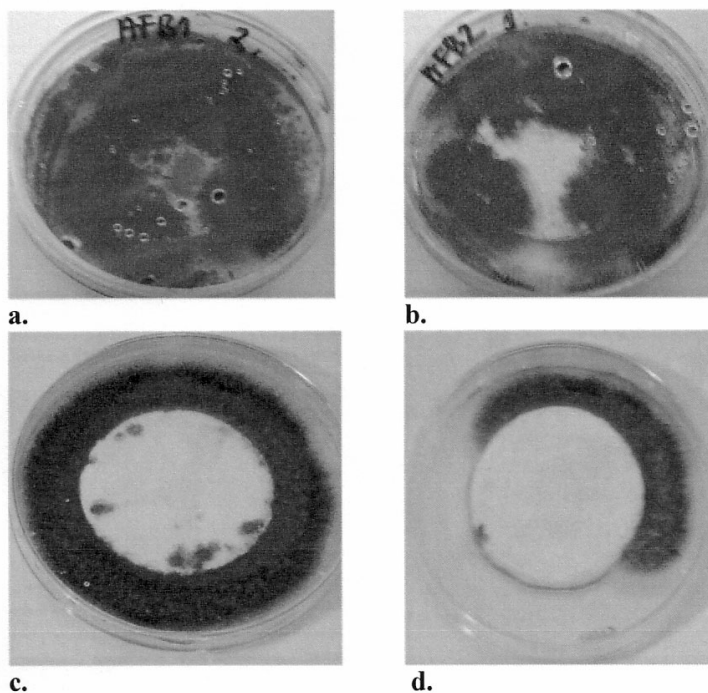


Photo 2. The appearance of emulsion paint with 1.5% (a and c) and 3% (b and d) additive of Nanobent ZR1 on whole culture medium (a and b) and deficient culture medium (c and d) resulting from exposure to mould fungus *Aspergillus niger*

*Fot. 2. Wygląd farby emulsyjnej z 1,5% (a i c) i 3% (b i d) dodatkiem Nanobentu ZR1 na pożywcę pełnowartościowej (a i b) i niepełnowartościowej (c i d) w wyniku działania grzyba pleśniowego – *Aspergillus niger**

In the case of emulsion paint composition, in the presence of deficient culture medium (photo 2 c–d), much better biocidal effect of Nanobent ZR 1 additive against mould fungus *Aspergillus niger* was observed, even when the concentration was lower (1.5%). Around 94% of the disc surface was not infected by mould fungus *Aspergillus niger*. Only small clusters of the fungus were visible on the sides and fringes of the disc with the paint coating applied. It might have been due to penetrable surface resulting from shrinkage cracks occurred during drying of the composition.

Then the resistance of acrylic lacquer composition to *Aspergillus niger* fungus was tested on whole and deficient culture medium. At the start a test of resistance of the control sample (a disc coated with acrylic lacquer without additives – photo 3a) was carried out, and then the resistance of the composition with an additive of Nanobent ZR1 (photo 3b–c) was tested. As it might have been expected, the lacquer coating without the additive of modified bentonite was not much resistant to the attack of microorganisms and the whole surface was covered by the growth of the mould fungus.

Based on the test results presented in photos 3b and 3c it was observed that the resistance to mould fungus *Aspergillus niger* in the case of acrylic lacquer composition with a 1.5% additive of Nanobent ZR1 (photo 3b) on whole culture medium was unsatisfactory – around 70% of the disc surface was covered by the mould fungus. A significant improvement of those properties was observed in the case of composition with a 3% content of Nanobent ZR1 additive (photo 3c), where areas infected with the mould fungus were present on the surface of the painted disc only in the amount of ~30%. In the case of testing the acrylic lacquer composition resistance to mould fungus growth in the presence of deficient culture medium (photo 4.) the growth of that mould fungus was assessed in accordance with standard to have been 1.3 in the case of a 1.5% additive of Nanobent ZR1 (photo 4a) and 0.5 in the case of a 3% content of Nanobent ZR1 agent (photo 4b), which was a very good result proving good biocidal properties of the additive used.

In the following stage of research a control test of resistance of mineral plaster (without any additive of nanofillers) to the mould fungi action was carried out. As it could have been expected, the test was unsuccessful. The whole surface of the gypsum disc with the plaster applied was covered by the fungus (photo 5a). Then the tests of the disc coated with the composition of mineral plaster with a 2% and a 4% additive of Nanobent ZR1 filler were carried out (photo 5 b, c and photo 6 a, b).

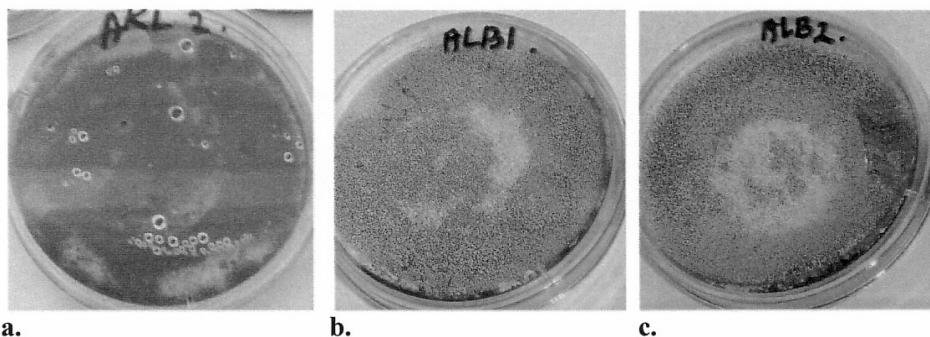


Photo 3. The appearance of: a – acrylic lacquer without the additive of, and b – with a 1.5% and c – with a 3% additive of Nanobent ZR1 filler as a result of the action of mould fungus *Aspergillus niger* on whole culture medium

Fot. 3. Wygląd: a – lakieru akrylowego bez dodatku oraz b – z 1,5% i c – z 3% dodatkiem napelnacza Nanobent ZR1, jako skutek działania grzyba pleśniowego – Aspergillus niger na pożywce pełnowartościowej

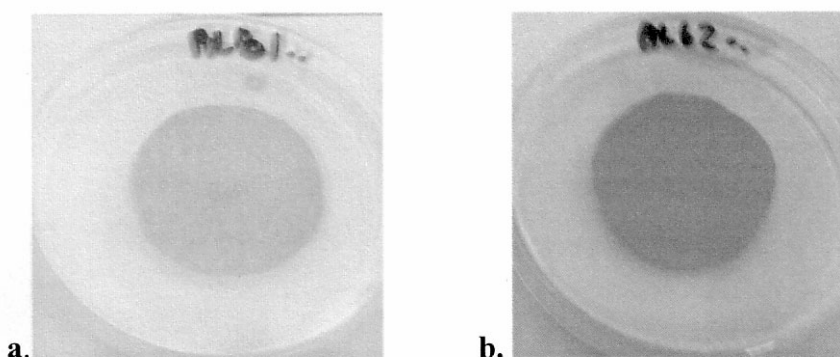


Photo 4. The appearance of acrylic lacquer with a 1.5% (a) and with a 3% (b) additive of Nanobent ZR1 agent as a result of the action of mould fungus *Aspergillus Niger* on deficient culture medium.

Fot. 4. Wygląd lakieru akrylowego z 1,5% (a) i 3% (b) dodatkiem środka Nanobent ZR1 na pożywce niepełnowartościowej, jako skutek działania grzyba pleśniowego Aspergillus Niger

Based on the obtained test results presented in photos 5 and 6 it was observed that the additive of Nanobent ZR1 agent had clear effect on inhibition of the growth of the mould fungi. A 1.5% additive of that product (photo 5b) was the reason why the bigger part of the surface, on which the composition was applied, was not covered by the fungus. In the case where a 3% additive of the tested Nanobent filler was added to the mineral plaster composition, a clear increase in inhibition of the fungus growth on the disc surface was visible. In that

case only small areas infected with mould fungus *Aspergillus niger* occurred. Probably it was a result of local leakiness in the coating applied on the disc.

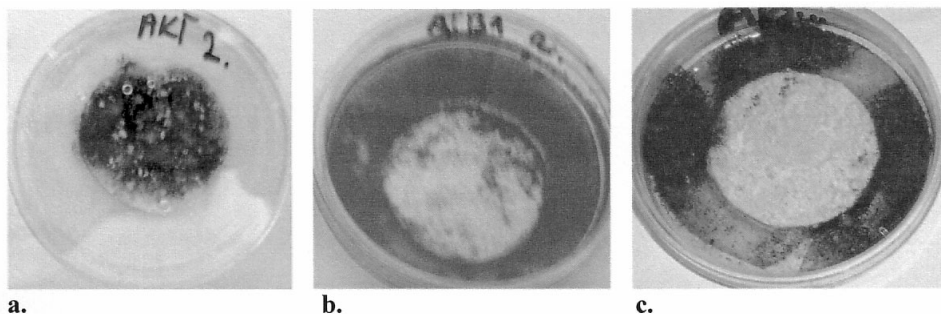


Photo 5. The appearance of: a – mineral plaster without the additive of, b – with a 1.5% and c – with a 3% additive of nanofiller Nanobent ZR1 as a result of the action of mould fungus *Aspergillus niger* on whole culture medium

*Fot. 5. Wygląd: a – tynku mineralnego bez dodatku, b – z 1,5% i c – 3% dodatkiem nanonapełniacza Nanobent ZR1, jako skutek działania grzyba pleśniowego – *Aspergillus niger* na pożywce pełnowartościowej*

During the tests of the resistance of mineral plaster to the mould fungus on deficient culture medium (photo 6) a clear inhibition of the mould fungus growth resulting from addition of Nanobent ZR1 nanofillers to the tested plaster was observed, and it may be considered a satisfactory result.

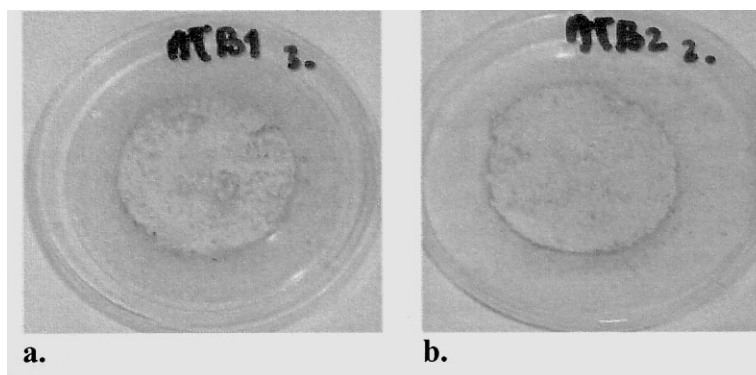


Photo 6. The appearance of mineral plaster with a 1.5% (a) and a 3% (b) additive of Nanobent ZR1 agent as a result of the action of mould fungus *Aspergillus niger* on deficient culture medium

*Fot. 6. Wygląd tynku mineralnego z 1,5% (a) i 3% (b) dodatkiem środka Nanobent ZR1 na pożywce niepełnowartościowej w wyniku działania grzyba pleśniowego – *Aspergillus niger**

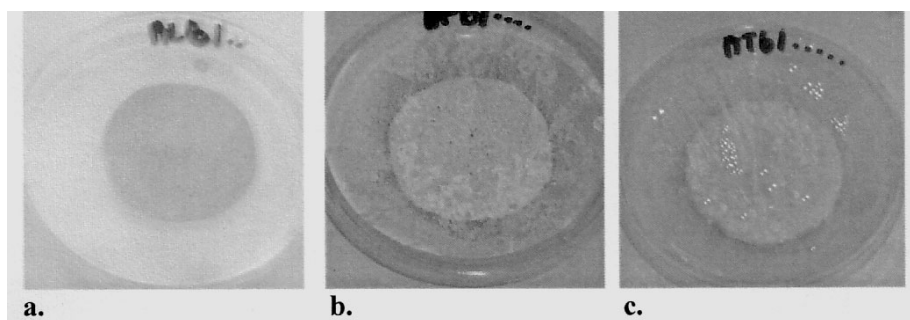


Photo 7. The appearance of coating made of acrylic lacquer (a), emulsion paint (b) and mineral plaster (c) with a 3% additive of Nanobent ZR2 nanofiller after incubation of mould fungus *Aspergillus niger* on whole culture medium

*Fot. 7. Wygląd powłoki wykonanej z lakieru akrylowego (a), farby emulsyjnej (b) i tynku mineralnego (c) z 3% dodatkiem nanonapełniaczy Nanobent ZR2 po inkubacji grzyba pleśniowego – *Aspergillus niger* na pożywce pełnowartościowej*

The second part of the experiments was devoted to testing of the resistance of selected compositions to the other mould fungus species, i.e. *Penicillium chrysogenum*. Based on the obtained test results it was observed that the results of those tests were identical with the above-described results obtained for the compositions exposed to mould fungus *Aspergillus N*.

To recapitulate, it may be stated that the results of the tests of the resistance of the tested compositions containing bentonite Nanobent ZR1 to mould fungi *Aspergillus niger* and *Penicillium chrysogenum* did not allow an unambiguous confirmation that the additive of that modified aluminosilicate influenced inhibition of the mould fungi growth. Thereby another type of modified bentonite called Nanobent ZR2, also produced by ZGM Zębiec, seated in Zębiec near Starachowice, was selected for tests. Due to the fact that the best results were obtained for a 3% additive of Nanobent ZR1 agent, the same concentration of the second of the nanofillers was used in further tests. The test results are given in table 1. Based on the obtained results it was observed that the additive of Nanobent ZR2 nanofiller to emulsion paint, acrylic lacquer and mineral plaster has a clear effect on improvement of the tested compositions' resistance to fungi. Chosen results are presented in photo 7, in which it can be seen that the whole surface of the gypsum disc on which coatings of acrylic lacquer, emulsion paint and mineral plaster containing the additive of Nanobent ZR2 agent were applied, practically was free from infection with the mould fungus. That resistance was observed even in conditions as favourable to fungus growth, as they can be on whole culture medium with the additive of glucose.

It should be mentioned here, that in the case of all samples, where emulsion paint, acrylic lacquer and mineral plaster containing the additive of Nanobentu

ZR2 were used, the results of the tests of the resistance to the action of the above-mentioned mould fungi were identical.

Conclusions

1. The presence of modified Nanobent nanofillers adds biocidal properties to the compositions of water-dilutable paints and lacquers, and mineral plasters in comparison with the above-mentioned compositions without the additive of modified Nanobent nanofillers.
2. The additive of a product of the trade name Nanobent ZR2 to the compositions of water-dilutable paints and lacquers, and mineral plasters had clearly better effect on inhibition of the mould fungi growth than the additive of Nanobent ZR1 product.

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WPLYW BENTONITÓW MODYFIKOWANYCH CZWARTORZĘDOWYMI SOLAMI AMONIOWYMI NA WŁAŚCIWOŚCI BIOBÓJCZE KOMPOZYCJI FARB I LAKIERÓW WODOROZCIEŃCZALNYCH ORAZ TYNKÓW MINERALNYCH

Streszczenie

Celem niniejszej pracy było otrzymanie kompozycji farb i lakierów akrylowych oraz tynków mineralnych z 1,5 i 3,0 % dodatkiem bentonitów Nanobent ZR1 i ZR2 (bentonitów modyfikowanych dwiema różnymi IV-rz. solami amoniowymi), które zostały wdrożone do produkcji w ZGM Zębiec w ramach grantu celowego nr 03933/C ZR7-6/2007. Powłoki uzyskane z użyciem tych kompozycji zbadano pod kątem odporności na działanie grzybów pleśniowych *Aspergillus niger* i *Penicillium chrysogenum* zgodnie z zaleceniami polskiej normy PN-EN ISO 846.

Zbadano odporność farby emulsyjnej (fot. 1), lakieru akrylowego oraz tynku mineralnego bez dodatku modyfikowanych bentonitów na działanie grzybów pleśniowych: *Aspergillus niger* oraz *Penicillium chrysogenum*. Następnie przeprowadzono badania wpływu dodatku środka Nanobent ZR1 na zahamowanie wzrostu grzybów pleśniowych w kompozycjach z farbą i lakierem akrylowym oraz tynkiem mineralnym (fot. 2–6). Zbadano również odporność podłoża (krążków gipsowych) na działanie grzybów pleśniowych (fot. 1).

Ponieważ najlepsze rezultaty uzyskano dla 3% dodatku nanonapełniacza Nanobent ZR1 (fot. 2–6), stąd w dalszych badaniach biobójczej skuteczności środka Nanobent ZR2 stosowano takie samo stężenie. Otrzymane wyniki badań zestawiono w tabeli 2 i na fot. 7. Na ich podstawie stwierdzono, że najlepsze rezultaty uzyskano dla kompozycji z 3% dodatkiem produktu Nanobent ZR2, gdzie praktycznie nie zaobserwowano wzrostu grzybów pleśni pleśniowych, nawet w obecności pożywki pełnowartościowej (z glukozą).

Słowa kluczowe: farba emulsyjna akrylowa, lakier akrylowy, tynk mineralny, czwartorzędowe sole amoniowe, właściwości biobójcze, *Aspergillus niger*, *Penicillium chrysogenum*