

MARIUSZ OLEKSY<sup>\*)</sup>, KATARZYNA LECKA-SZLACHTA, MACIEJ HENECZKOWSKI,  
HENRYK GALINA

Rzeszow University of Technology  
Faculty of Chemistry  
ul. W. Pola 2, 35-959 Rzeszow, Poland

## The effect of modified bentonites on the thixotropic properties of coating materials and their resistance against mold fungi settlement

**Summary** — Biostatic and thixotropic properties of bentonites modified with quaternary ammonium salts (QAS) in a waterborne paint and acrylic lacquer are presented. The fungistatic properties were tested for two commercially available bentonites modified with QAS. The bentonites were added to emulsion acrylic paint and acrylic lacquer in the amount of 2 or 4 wt. %. The resulting compositions were put on gypsum plaster disks and treated with *Aspergillus niger* and *Penicillium chrysogenum*, the molds frequently met in human environments. Microbiological tests were performed using procedures consistent with Polish Standards with modifications which stemmed from the materials used. The presence of bentonites modified with QAS substantially improved the resistance of coatings against microorganism colonization. Thixotropic properties of paint compositions containing modified bentonites were also found improved.

**Keywords:** emulsion acrylic paint, acrylic lacquer, bentonites, quaternary ammonium salts, *Aspergillus niger*, *Penicillium chrysogenum*, antifungal activity.

WPLYW MODYFIKOWANYCH BENTONITÓW NA WŁAŚCIWOŚCI TIKSOTROPOWE MATERIAŁÓW POWŁOKOWYCH ORAZ NA ODPORNOŚĆ NA DZIAŁANIE GRZYBÓW

**Streszczenie** — Zbadano wpływ dodatku do kompozycji farby emulsyjnej lub lakieru akrylowego, bentonitów modyfikowanych IV-rz. solami amoniowymi (QAS), na właściwości hamujące rozwój grzybów. Oceniano grzyboodporność dwóch handlowych bentonitów: Specjal i SN, modyfikowanych wybranymi handlowymi QAS (tabele 1, 2), dodawanymi do farby lub lakieru w ilości 2 lub 4 % mas. Przygotowane kompozycje nanoszono na krążki gipsowe i poddawano działaniu, najczęściej występujących w środowisku człowieka grzybów pleśniowych *Aspergillus niger* oraz *Penicillium chrysogenum*. Badania mikrobiologiczne prowadzono według wytycznych polskiej normy z pewnymi modyfikacjami wynikającymi ze specyfiki badanych materiałów (tabela 3). Najlepsze właściwości grzybostatyczne wykazywały bentonity modyfikowane QAS Bardac LF oraz Bardac 22, co jest konsekwencją ich budowy chemicznej (tabele 4, 5, rys. 2, 3). Oznaczano także wpływ dodatku modyfikowanych bentonitów na właściwości tiksotropowe badanych kompozycji (tabela 6).

**Słowa kluczowe:** farba akrylowa, lakier akrylowy, bentonity, czwartorzędowe sole amoniowe, *Aspergillus niger*, *Penicillium chrysogenum*, aktywność grzybobójcza.

### INTRODUCTION

Waterborne coating materials, particularly those containing phospholipids (lecithin), proteins (casein) or polysaccharides (cellulose or starch derivatives) used for thickening are often sensitive to microbiological attack [1]. The same applies to coatings already applied on a surface, particularly in humid environment. Current standards in civil engineering, and the needs of energy saving, may cause insufficient ventilation, due to air tight

walls and fully closed openings. This favours a built-up of humidity and provides suitable conditions for microorganisms to grow. Hence, the thickeners based on natural products are recently replaced by modified bentonites [2].

Microbiological attack on waterborne coatings may change their properties such as viscosity, colour, pH and may even lead to gas emission, unpleasant smell, precipitation, and gelation [3]. In order to prevent the microorganism growth in painting materials and on painted surfaces, certain biocides are used to hinder life functions by blocking the reproduction mechanisms in microorga-

<sup>\*)</sup> Author for correspondence; e-mail: molek@prz.edu.pl

nism cells [4–7]. Various biocides have been developed and applied in waterborne coatings [8–10]. Among them are organic compounds effectively disturbing living processes in microorganisms, such as phenolic derivatives [11–13], aliphatic hydrocarbons [14–17], and aliphatic compounds containing sulphur and/or nitrogen [18–23]. An interesting solution was the application of zeolites slowly releasing silver ions. Silver ions are known to distract the cells ability to produce the enzymes which take part in energy acquiring processes. The effect is the loss of ability of microorganisms to develop and reproduce [24–26]. Another advantage of silver ions is that microorganisms are unable to develop resistance to its action. In this respect silver differs from the organic biocides.

This work is a continuation of our studies on the applications of modified bentonites as fillers, thickeners, and strengthening agents for polymer compositions [27–33]. Here, we present the results of using modified bentonites as fungistatic agents. The advantage is taken of the presence of quaternary ammonium salts (QAS) in the modified bentonites. QAS's are also known as having biocidal properties, provided the appropriate groups are used as nitrogen substituents [34]. At the same time the modified bentonites substantially improve thixotropic properties of coating compositions.

## EXPERIMENTAL

### Materials

– The bentonites used are listed in Table 1. All were produce by Zebiec S.A. Starachowice, Poland.

– Quaternary ammonium salts (QAS) are presented in Table 2. All were supplied by LONZA, Switzerland.

**Table 1. Natural bentonites used in this work**

Characterization	Bentonite SN	Bentonite Specjal (S)
Montmorillonite, wt. %	95	90
Carbonates, wt. %	<5	≤5
Water, wt. %	<5	≤5

**Table 2. Quaternary ammonium salts (QAS) of general formula  $R_1R_2R_3R_4N^+Cl^-$  used in this work**

QAS commercial name	$R_1$	$R_2$	$R_3$	$R_4$
Bardac LF	$C_8H_{17}$	$CH_3$	$CH_3$	$C_8H_{17}$
Barquat CB50	$PhCH_2$	$CH_3$	$CH_3$	$C_{12}H_{25}$
Bardac 22	$C_{12}H_{25}$	$CH_3$	$CH_3$	$C_{12}H_{25}$

– Polyethylene glycol (producer ROTH) was used as a wetting agent.

– The nutritional salt/agarose medium with glucose contained in 1000 cm<sup>3</sup>: NaNO<sub>3</sub> 2 g; KH<sub>2</sub>PO<sub>4</sub> 0.7 g; K<sub>2</sub>HPO<sub>4</sub>

0.3 g; KCl 0.5 g; MgSO<sub>4</sub> · 7 H<sub>2</sub>O; agar 20 g; glucose 30 g; pH = 6.0–6.5. It was autoclaved under standard conditions: 121 °C for 45 min.

– The non-nutritional salt/agar medium without glucose contained in 1000 cm<sup>3</sup>: NaNO<sub>3</sub> 2 g; KH<sub>2</sub>PO<sub>4</sub> 0.7 g; K<sub>2</sub>HPO<sub>4</sub> 0.3 g; KCl 0.5 g; MgSO<sub>4</sub> · 7 H<sub>2</sub>O; agar 20 g; pH = 6.0–6.5. It was autoclaved as above. The salts were reagent grade.

– *Aspergillus niger*, MERCK, ATCC 16404.

– *Penicillium chrysogenum*, MERCK, ATCC 10106.

– Waterborne coating based on an acrylic emulsion as well as acrylic varnish (ethyl acetate solution) from Śniezka, Poland. The samples containing no tixotropic and bioactive additives were supplied on our special request.

– Sticking gypsum plaster, Nowa Doliny Nidy, Poland.

### Modification of bentonites with quaternary ammonium salts

In this work we made use of a method of modification of natural bentonites that was already described [28–33].

The degree of modification of bentonites was relatively high (28 to 35 g of QAS per 100 g of neat bentonite). The bentonites were dried after modification at 40–60 °C, initially in a convection oven and then in a vacuum oven. The product was ground to the grain size not exceeding 0.07 mm.

In order to assess the effects of modification, the products were examined using differential scanning calorimetry (DSC) and X-ray diffraction method. Both methods confirmed intercalation of mineral layers by QAS. The results of the measurements were described elsewhere [31–33].

### Methodology

#### The procedure of studying the resistance against mold fungi

Commercial emulsion acrylic paint (P) and acrylic lacquer (L) were supplied by the producer without any biocides. Bentonites modified with QAS were added to these products in the amount of 2 wt. % or 4 wt. %. These were then homogenized for 5 min in the coating compositions by using a laboratory mixer rotating at 1000 rpm. Each composition was put on a plaster disk of 30 mm diameter and 2–3 mm thick (twice, day after day, in two layers each time). Plaster disks were then placed horizontally onto Petri's dish containing agar nourishment media, one with glucose and another without it. Central parts of plaster disks were inoculated with spore suspension containing *Aspergillus niger* or *Penicillium chrysogenum*. The amount used was 0.1 cm<sup>3</sup> of aqueous spore suspension containing 1.0 · 10<sup>6</sup> CFU cm<sup>-3</sup> and incubated for 28 days at 29 °C ± 1 °C, with humidity 95 %. The spore suspension contained polyethylene glycol as a wetting

**Table 3. Rating of mold growth according to a normative procedure (PN-EN ISO 846)**

Rating of growth intensity	Assessment of observed growth on specimens (sporulating or non-sporulating, or both)
0/0	no growth on specimen and on medium is seen; must be confirmed by microscopic examination
0/1	growth of mold on specimen seen only under microscope
0+	no growth on specimen is seen under microscope, inhibition zone formed on the medium around specimen
(0)	no growth on specimen seen under microscope, medium is overgrown by mold up to specimen edges
1	traces of mold growth on specimen with edges overgrown by sporulated spawn
2	small growth of mold on specimen seen with less than 5 % of surface infected
3	noticeable growth seen with naked eye with 5 % to 25 % of specimen surface covered by spawn
4	growth seen with naked eye with more than 25 % of specimen surface covered by spawn
5	growth well seen with naked eye with more than 50 %, but less than 75 % of specimen surface covered by spawn
6	growth well seen with naked eye with more than 75 % of specimen surface covered by spawn

agent added to stabilize cytoplasmic membrane of the spores. Each hindering of mold growth on the plaster disks and on the medium indicated the fungistatic effects including the inhibition of spores' germination of the modified bentonite. The extent of fungi growth was first estimated with macroscopic observation. When necessary an optical microscope was used (magnification 40×). A photographic documentation was also made. The photographs were additionally examined to evaluate the surface area of infected part of plaster discs by using AutoCAD.

The growth of mold was assessed as in Table 3. If the results from one set of samples were different by more than two in the adopted rating scale, the tests were redone with new samples. At least 20 samples of each system were prepared. The data in Table 3 contain average results from all experiments.

Microbiological tests were performed using procedures consistent with PN-EN ISO 846.

### Thixotropic properties of coating compositions

A simple measure of thixotropic properties of a liquid is the ratio of its viscosities at two different shear rates, typically determined in a rotational viscometer at two rotation rates: 5 and 50 rpm. The thixotropy index (*IT*) of the compositions is calculated from the equation:

$$IT = \frac{\eta_5}{\eta_{50}} \quad (1)$$

where:  $\eta_5$  and  $\eta_{50}$  – the viscosities obtained at the rotation rates 5 and 50  $\text{min}^{-1}$ , respectively.

The measurements were carried out using a Brookfield RDV2 rotational viscometer at  $25 \pm 1$  °C. Rotor no. 2 was used (PN-73/C-81547). Half an hour break between each measurement was applied in order to let the structure to rebuild.

## RESULTS AND DISCUSSION

We start the discussion with plaster disks put on Petri's dish with medium containing glucose and inocu-

lated with spores *Aspergillus niger*. Samples were incubated for 28 days. After incubation, the whole plaster disk was found overgrown by mold *A. niger* (Fig. 1., Table 4). We have found that in the experiments the plaster was an ideal material for mold incubation. The reason was that plaster with its capillary structure promotes migration of medium into the disk and greatly facilitates the

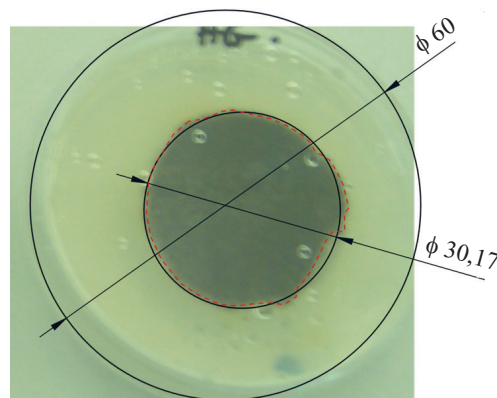


Fig. 1. The AutoCAD supported procedure for measuring the proportion of a plaster disk infected by a mold fungus. Here, *Aspergillus niger*'s growth is shown on plain plaster disk in the nutrient agar with glucose. The infected surface (encircled with red broken line) was here related to the plaster disc surface (radius 30.17 mm)

growth of molds. Then, the resistance of unmodified paint against mold infection was assessed (reference sample). The surface of plaster disks covered with plain paint (not modified with bentonite) was very quickly overgrown by mold (Table 4).

In further experiments, the resistance of coatings containing bentonites modified with quaternary ammonium salts were examined. The bentonites were used in the amount of 2 or 4 wt. %.

The plaster disks coated with emulsion acrylic paint containing bentonites modified with QAS Barquat CB50

Table 4. The results of growth inhibition measurements for *A. niger* on samples with paint and lacquer<sup>\*)</sup>

No.	Type of coating on plaster put into salt-agar medium	Nutrition medium with glucose			Average surface area of disc infected by mold fungus, %	Non-nutrition medium without glucose			Average surface area of disc infected by mold fungus, %
		rating of mold growth				rating of mold growth			
		min	max	average		min	max	average	
1	Plain plaster (specimen)	6.0	6.0	6.0	100.0	4.0	4.0	4.0	66.7
2	Paint without additives	6.0	6.0	6.0	100.0	5.0	5.0	5.0	83.3
3	Paint + 2 % bentonite S QAS CB50	5.0	6.0	5.7	94.7	1.0	1.0	1.0	16.6
4	Paint + 4 % bentonite S QAS CB50	4.0	5.0	4.7	78.4	0.0	1.0	0.5	8.3
5	Paint + 2 % bentonites SN QAS CB50	6.0	6.0	6.0	100.0	1.0	1.0	1.0	16.5
6	Paint + 4 % bentonites SN QAS CB50	5.0	6.0	5.5	91.6	0.0	0.0	0.0	0.0
7	Paint + 2 % bentonite S QAS B-22	1.0	3.0	2.0	33.3	0.5	1.0	0.8	13.3
8	Paint + 4 % bentonite S QAS B-22	0.5	2.0	1.3	21.3	0.0	1.0	0.6	10.1
9	Paint + 2 % bentonite S QAS B-LF	3.5	4.5	4.0	66.7	0.5	1.0	0.9	14.9
10	Paint + 4 % bentonite S QAS B-LF	2.5	3.5	2.9	48.3	0.5	1.0	0.7	11.2
11	Paint + 2 % bentonite SN QAS B-22	1.0	3.0	2.2	36.6	0.5	1.0	0.8	13.2
12	Paint + 4 % bentonite SN QAS B-22	0.5	2.0	1.5	25.2	0.0	1.0	0.6	10.2
13	Paint + 2 % bentonite SN QAS B-LF	3.5	4.5	4.4	73.3	0.5	1.0	0.9	15.0
14	Paint + 4 % bentonite SN QAS B-LF	2.5	3.5	3.1	51.6	0.5	1.0	0.7	11.1
15	Lacquer without additives	6.0	6.0	6.0	100.0	3.0	4.0	3.7	61.6
16	Lacquer + 2 % bentonite S QAS CB50	5.0	5.0	5.0	83.3	1.0	2.0	1.3	21.6
17	Lacquer + 4 % bentonite S QAS CB50	4.0	5.0	4.3	71.6	0.0	1.0	0.5	8.2
18	Lacquer + 2 % bentonite SN QAS CB50	4.0	6.0	5.3	88.3	1.0	1.0	1.0	16.4
19	Lacquer + 2 % bentonite SN QAS CB50	4.0	5.0	4.2	70.0	0.0	1.0	0.5	8.3
20	Lacquer + 2 % bentonite S QAS B-22	0.5	2.5	1.5	25.1	0.0	0.5	0.2	3.4
21	Lacquer + 4 % bentonite S QAS B-22	0.5	2.0	1.1	18.3	0.0	0.0	0.0	0.0
22	Lacquer + 2 % bentonite S QAS B-LF	2.5	3.5	3.2	52.4	0.0	0.5	0.3	5.1
23	Lacquer + 4 % bentonite S QAS B-LF	2.0	3.0	2.5	41.6	0.0	0.0	0.0	0.0
24	Lacquer + 2 % bentonite SN QAS B-22	0.5	2.5	1.6	26.6	0.0	0.5	0.3	5.0
25	Lacquer + 4 % bentonite S QAS B-22	0.5	2.0	1.2	20.1	0.0	0.0	0.0	0.0
26	Lacquer + 2 % bentonite S QAS B-LF	2.5	3.5	3.3	55.1	0.0	0.5	0.3	5.2
27	Lacquer + 4 % bentonite S QAS B-LF	2.0	3.0	2.6	43.2	0.0	0.5	0.1	1.6

<sup>\*)</sup> The commercial names of quaternary ammonium salts (QAS) modifying natural bentonites Specjal (S) and SN are abbreviated to CB 50, B-22 and B-LF for the products Barquat CB 50, Bardac 22, and Bardac LF, respectively. The average values are shown from at least six samples.

had, after incubation with *Aspergillus niger*, over 95 % of disk surface infected by the fungi.

Similar results were obtained by testing the resistance of the acrylic lacquer against the same spore *Aspergillus niger*. The results in Table 4 indicate the lack of resistance of incubated plaster disks covered by unmodified lacquer. The incubation was carried out using both nutrient and non-nutrient media. In all cases the plaster disks were substantially covered by fungi lawn. Somewhat better, but still not satisfactory results were obtained for the varnish containing 4 wt. % of bentonites modified with QAS CB50.

In the second part of our studies we tested our compositions against another mold: *Penicillium chrysogenum*. As in the case of *A. niger*, plaster disks alone were checked first (reference samples). Whole surface was found covered by mold after incubation. Then, disks coated with

paint or varnish in different combinations with QAS CB50 modified bentonites (S or SN, 2, or 4 wt. %) were tested. Unfortunately, in all samples the inhibition of growth was insufficient as one can conclude from the results collected in Table 5.

Evidently, the quaternary ammonium salts containing two methyl, dodecyl and benzyl substituents did not furnish the bentonites with sufficient fungistatic. On the other hand, the quaternary ammonium salts containing purely hydrocarbon substituents at nitrogen atom are known for their disinfection activity. Hence, we next tried QAS's Bardac 22 and Bardac LF (see Table 2) expecting somewhat better biocidal action from these compounds, even when used indirectly as bentonite modifiers.

Indeed, bentonites S and SN modified with Bardac 22 ammonium salt, substantially hindered growth of both

Table 5. The results of growth inhibition measurements for *P. chrysogenum* on samples with paint or varnish<sup>\*)</sup>

No.	Type of coating*	Medium with glucose			Average surface area of disc infected by mold fungus, %	Medium without glucose			Average surface area of disc infected by mold fungus, %
		rating of mold growth				rating of mold growth			
		min	max	average		min	max	average	
1	Plain plaster	6.0	6.0	6.0	100.0	4.0	4.0	4.0	66.5
2	Paint without additives	6.0	6.0	6.0	100.0	5.0	5.0	5.0	83.3
3	Paint + 2 % bentonite S QAS CB50	6.0	6.0	6.0	100.0	1.0	1.0	1.0	16.6
4	Paint + 4 % bentonite S QAS CB50	4.0	4.0	4.0	66.6	0.0	0.0	0.0	0.0
5	Paint + 2 % bentonite SN QAS CB50	6.0	6.0	6.0	100.0	1.0	1.0	1.0	16.5
6	Paint + 4 % bentonite SN QAS CB50	4.0	6.0	5.2	86.6	0.0	1.0	0.5	8.3
7	Paint + 2 % bentonite S QAS B-22	0.5	2.0	1.4	23.3	0.5	1.0	0.6	10.1
8	Paint + 4 % bentonite S QAS B-22	0.0	1.5	0.9	15.1	0.0	0.5	0.3	5.1
9	Paint + 2 % bentonite S QAS B-LF	3.0	4.0	3.7	61.6	0.5	1.0	0.7	11.6
10	Paint + 4 % bentonite S QAS B-LF	2.0	3.5	2.9	48.3	0.5	1.0	0.6	10.2
11	Paint + 2 % bentonite SN QAS B-22	0.5	2.0	1.5	25.1	0.5	1.0	0.6	10.1
12	Paint + 4 % bentonite SN QAS B-22	0.0	1.5	1.1	18.3	0.0	0.5	0.4	6.5
13	Paint + 2 % bentonite SN QAS B-LF	3.5	4.5	4.4	73.3	0.5	1.0	0.7	11.5
14	Paint + 4 % bentonite SN QAS B-LF	2.5	3.5	3.1	51.6	0.0	1.0	0.7	11.6
15	Lacquer without additives	6.0	6.0	6.0	100.0	3.0	4.0	3.7	61.6
16	Lacquer + 2 % bentonite S QAS CB50	4.0	5.0	4.3	71.6	0.0	0.0	0.0	0.0
17	Lacquer + 4 % bentonite S QAS CB50	4.0	5.0	4.1	68.3	0.0	0.0	0.0	0.0
18	Lacquer + 2 % bentonite QAS CB50	4.0	5.0	4.3	71.5	0.0	1.0	0.5	8.2
19	Lacquer + 2 % bentonite SN QAS CB50	4.0	4.0	4.0	66.5	0.0	0.0	0.0	0.0
20	Lacquer + 2 % bentonite S QAS B-22	0.5	1.5	0.7	11.6	0.0	0.0	0.0	0.0
21	Lacquer + 4 % bentonite S QAS B-22	0.0	1.0	0.6	10.1	0.0	0.0	0.0	0.0
22	Lacquer + 2 % bentonite S QAS B-LF	1.5	3.0	2.7	45.1	0.0	0.5	0.2	3.3
23	Lacquer + 4 % bentonite S QAS B-LF	1.0	2.5	2.1	35.1	0.0	0.0	0.0	0.0
24	Lacquer + 2 % bentonite SN QAS B-22	0.0	1.5	1.1	18.2	0.0	0.0	0.0	0.0
25	Lacquer + 4 % bentonite SN QAS B-22	0.0	1.0	0.6	10.2	0.0	0.0	0.0	0.0
26	Lacquer + 2 % bentonite SN QAS B-LF	1.5	3.0	2.8	46.6	0.0	0.5	0.3	5.1
27	Lacquer + 4 % bentonite SN QAS B-LF	1.0	2.5	2.3	38.3	0.0	0.0	0.0	0.0

<sup>\*)</sup> The commercial names of quaternary ammonium salts (QAS) modifying natural bentonites Specjal (S) and SN are abbreviated to CB 50, B-22 and B-LF for the products Barquat CB 50, Bardac 22, and Bardac LF, respectively. The average values are from at least six samples.

*Aspergillus niger* and *Penicillium chrysogenum* when used as components of emulsion acrylic paint or acrylic lacquer, even at the smaller amount of 2 wt. %. This biostatic activity was observed for coated plaster disks incubated both in non-nutrient and in nutrient glucose containing medium. Slightly worse, but still positive results were also obtained for bentonites modified with Bardac LF ammonium salt. The results are illustrated in Figs. 2 and 3 and listed in Tables 4 and 5.

The reason might be that bentonites modified with QAS Bardac 22 and Bardac LF, both lacking the benzyl substituent, are less hydrophobic than Barquat CB50 and make bentonite particles better solvated and dispersed in emulsion acrylic paint and acrylic lacquer.

It appears that the biostatic activity of Bardac 22 (which is used as a precursor of disinfecting agents) is particularly favoured by its specific structure.

The results in Tables 4 and 5 clearly indicate that the conclusions from visual assessment made according to the standard procedures (*cf.* Table 3) are in very good agreement with the numerical data obtained by using the AutoCAD based calculations.

#### Thixotropic properties of emulsion acrylic paints and acrylic varnishes containing modified bentonites

Bentonites are known from literature and from our previous studies as efficient thixotropic agents. Hence, it was of interest to study the effect of modified bentonites on the rheological properties of containing them the emulsion acrylic paint and acrylic varnish. The thixotropy index (*IT*) of the compositions was calculated from equation (1). The results are listed in Table 6.

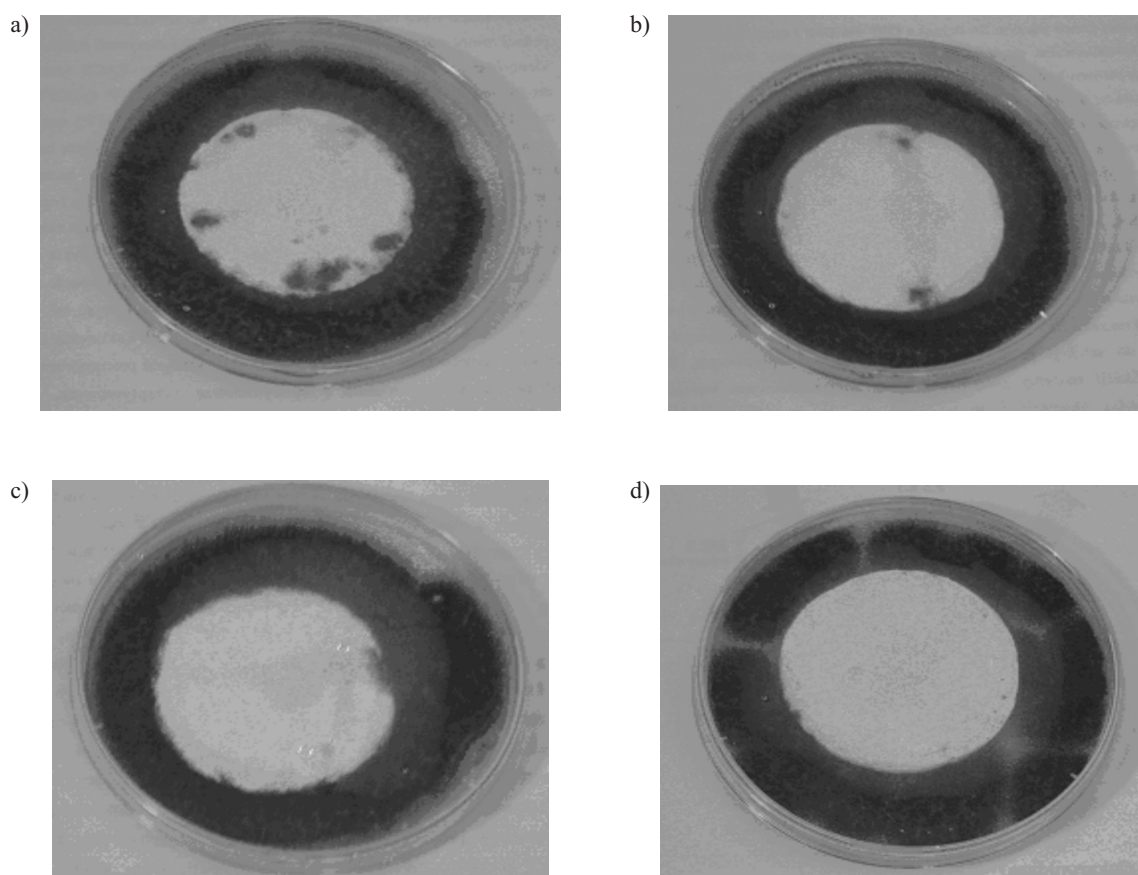


Fig. 2. *Aspergillus niger*'s growth in medium with glucose on plaster disks coated with emulsion acrylic paint containing: A, B: 2 or 4 wt. % of bentonite S modified with QAS Bardac LF, respectively; C, D: 2 or 4 wt. % of bentonite S modified with QAS Bardac 22, respectively

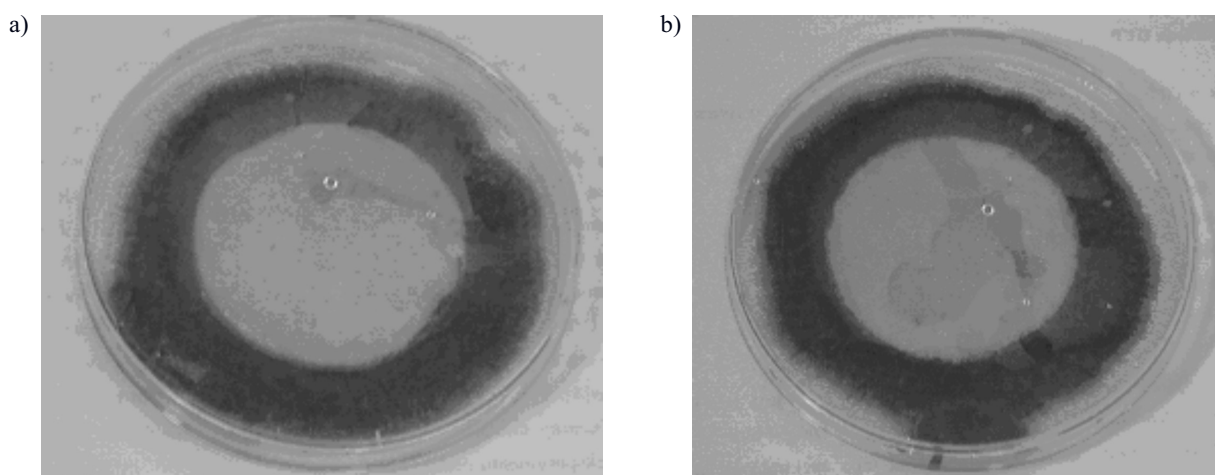


Fig. 3. *Penicillium chrysogenum*'s growth in medium with glucose on the plaster disk coated with: A, B: acrylic lacquer with 2 and 4 wt. %, respectively, of QAS Bardac LF modified bentonite S

As can be seen the compositions containing bentonites modified with QAS Bardac 22 or Bardac LF (with aliphatic substituents, only) exhibit better thixotropic properties than compositions containing Barquat CB50 modifier. In the latter, one substituent is benzyl group. The all aliphatic QAS modified bentonites provide compositions with much better thixotropic properties than unmodified bentonites. This behavior of the compositions might be

related to differences in hydrophobicity of the QAS modifiers. Benzyl substituent probably enhances hydrophobic character of bentonites, thus leading to its poorer dispersion in the waterborne products.

It is interesting to examine the effect of the amount of bentonite and kind of QAS substituent groups on the thixotropy index (*TI*). The highest values of *TI* were measured for the compositions containing 4 wt. % of bento-

nite SN or Specjal (S) modified with QAS Bardac 22 (two methyl and two dodecyl groups).

**Table 6.** The results of thixotropy index (IT) measurements for the compositions of acrylic varnish and emulsion paint<sup>\*)</sup>

Composition	Thixotropy index IT at 5/50 rpm	
	bentonite content wt. %	
	2	4
Acrylic lacquer + bentonite S	2.15	3.05
Acrylic lacquer + bentonite S QAS CB50	1.28	1.83
Acrylic lacquer + bentonite S QAS B-LF	3.12	4.21
Acrylic lacquer + bentonite S QAS B-22	3.43	4.50
Acrylic lacquer + bentonite SN	2.35	3.30
Acrylic lacquer + bentonite SN QAS CB50	1.42	1.95
Acrylic lacquer + bentonite SN QAS B-LF	3.33	4.29
Acrylic lacquer + bentonite SN QAS B-22	3.61	5.02
Emulsion paint + bentonite S	1.69	1.92
Emulsion paint + bentonite S QAS CB50	1.14	1.67
Emulsion paint + bentonite S QAS B-LF	3.09	4.78
Emulsion paint + bentonite S QAS B-22	3.14	5.11
Emulsion paint + bentonite S	1.70	2.04
Emulsion paint + bentonite SN QAS CB50	1.28	1.78
Emulsion paint + bentonite SN QAS B-LF	3.12	5.02
Emulsion paint + bentonite SN QAS B-22	3.32	5.67

<sup>\*)</sup> IT for plain acrylic lacquer: 0.15; for plain emulsion paint: 0.12.

## CONCLUSIONS

— The presence of bentonite modified with quaternary ammonium salts in compositions of a waterborne paint and varnish as well as in coating layers on mineral plasters noticeably reduces the growth of mold on the surface of disks. The best fungistatic properties against mold provide bentonites of commercial names Specjal and SN modified with quaternary ammonium salt Bardac 22 built of two methyl and two dodecyl groups.

— The chemical structure of substituents at nitrogen atom of QAS has an important effect on the thixotropic properties of paint compositions. The best results were obtained for compositions containing bentonites Specjal and SN modified with QAS Bardac 22.

## REFERENCES

1. Spychaj T., Spychaj S.: „Paints and Waterborne Adhesives” (in Polish), WNT, Warsaw 1996.

- Santiago F., Mucientes A. E., Osorio M., Rivera C.: *Eur. Polym. J.* 2007, **43**, 1.
- Gobbert Ch., Schichtel M., Nonninger R.: *Farbe Lack* 2002, **108**, 20.
- Shirakawa M. A., John V. M., Gaylarde C. C., Gaylarde P., Gambale W.: *Mater. Struct./Materiaux et Constructions* 2004, **37**, 472.
- Emtiazi G., Nahvi I., Salehbaig M.: *Res. Bull. Isfahan Univ.* 1999, **1**, 15.
- Emtiazi G.: *Poll. Res.* 2000, **19**, 31.
- Emtiazi G., Naghavi N., Bordbar A.: *Biodegradation* 2001, **12**, 259.
- Marini M., Boni M., Iseppi R., Toselli M., Pilati F.: *Eur. Polym. J.* 2007, **43**, 3621.
- Ranalli G., Zanardini E., Sorlini C.: „Encyclopedia of Microbiology”, Elsevier, Oxford 2009, pp. 191–205.
- Nohr R. S., MacDonald G. J.: *J. Biomater. Sci. Polym. Ed.* 1994, **5**, 607.
- Lin J., Murthy S. K., Olsen B. D., Gleason K. K., Klibanov A. M.: *Biotechnol. Lett.* 2003, **25**, 1661.
- Lin J., Qiu S., Lewis K., Klibanov A. M.: *Biotechnol. Bioeng.* 2003, **83**, 168.
- Jafra S., Łojkowska E.: *Biotechnologia* 1999, **2**(45), 94.
- Pat. PL* 1 934 473 B1 (2007).
- Pat. WO* 2 006 041 251 (2006).
- Pat. US* 6 468 521 (2002).
- Pat. WO* 206 026 026 (2006).
- Pat. Jap.* 60 202 162 (1985).
- Pat. Jap.* 11 263 704 (1999).
- Pat. GB* 1 036 404 (1966).
- Pat. Chin.* 1 616 559 (2005).
- Pat. Chin.* 1 730 581 (2006).
- Pat. DE* 4 226 222 (1990).
- Ślusarczyk A., Piotrkowska M.: *Polimery* 2008, **53**, 743.
- Xie Y., Krause A., Militz H., Mai C.: *Prog. Org. Coat.* 2006, **57**, 291.
- Tezel U., Pierson J. A., Pavlostathis S. G.: *Water Res.* 2006, **40**, 3660.
- Oleksy M., Galina H.: *Polimery* 1999, **44**, 430.
- Galina H., Oleksy M.: „Quaternary ammonium salts and their applications” (in Polish), Wyd. Inst. Techn. DREWNA, Poznań 2001, pp. 133–146.
- Oleksy M., Heneczkowski M.: *Polimery* 2005, **50**, 143.
- Oleksy M., Heneczkowski M., Galina H.: *J. Appl. Polym. Sci.* 2005, **96**, 793.
- Oleksy M., Heneczkowski M., Galina H.: *Polimery* 2007, **52**, 345.
- Pat. PL* 178 899 (2000).
- Pat. PL* 178 900 (2000).
- Oblak E., Gamian A.: *Postepy Hig. Med. Dosw.* 2010, **64**, 201.

Received 4 IV 2012.