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Silver as fungistatic agent in paints

Summary — Investigations described in the article were done to estimate antimicrobial properties of silver preparations in decorative, waterborne paints. Several commercially available preparations were used in the research. Tests were performed for silver concentrations of 30 ppm or 40 ppm (by weight, recounted per Ag) per paint, for coatings on glass, cardboard-plaster and lignin-cement plates, before and after accelerated ageing. Estimation of antimicrobial properties was performed according to PN-85/C-89080 with necessary modifications, resulting from the type of materials tested. *Aspergillus niger, Cladosporium cladosporioides, Aspergillus versicolor* and *Penicillium chrysogenum* isolated from the housing environment were used as test microorganisms. Results show fungistatic effectiveness of silver. This effect depends upon the type of coated surface, pH value of a surrounding media, type of moulds that inhabit the coating and upon the type of silver preparation.
Key words: antimicrobial properties, silver, dispersion paints, biocidal effectiveness.

SREBRO JAKO GRZYBOBÓJCZY DODATEK DO FARB

Streszczenie — W pracy przedstawiono wyniki badań właściwości biobójczych dekoracyjnych farb wodorozcieńczalnych, których właściwości przeciwdrobnoustrojowe są wynikiem oddziaływania srebra. Sprawdzano skuteczność biobójczą czterech handlowych preparatów srebra, dodawanych do farby podstawowej w ilości 30 ppm oraz 40 ppm (masowo, w przeliczeniu na Ag). Badano powłoki świeże oraz poddawane procesowi przyspieszonego starzenia. Powłoki uzyskane z przygotowanych farb nanoszono na trzy rodzaje podłoża: szkło, płytki lignino-cementowe lub płyty kartonowo-gipsowe. Badania mikrobiologiczne prowadzono według normy PN-85/C-89080 z własnymi modyfikacjami wynikającymi ze specyfiki badanych materiałów. W badaniach stosowano grzyby pleśniowe, najczęściej wykrywane w pomieszczeniach użytkowych tj. *Aspergillus niger, Cladosporium cladosporioides, Aspergillus versicolor* oraz *Penicillium chrysogenum*. Wymienione szczepy zostały wyizolowane ze środowiska mieszkaniowego. Stwierdzono, że srebro wykazuje działanie fungistatyczne, a efekt ten zależy od rodzaju podłoża, od pH środowiska, rodzaju zastosowanego preparatu srebra oraz od gatunku organizmu zasiedlającego powłokę.
Słowa kluczowe: srebro, działanie przeciwdrobnoustrojowe, farby dyspersyjne, skuteczność biobójcza.

Microorganisms need nutrients, optimum pH, moisture and light for growth and proliferation. These requirements, differ from species to species, as shown in Table 1 [1].

Bacteria, fungi and algae act in different ways. Bacteria cause changes invisible to human eye like changes in properties of contaminated materials (*e.g.* pH, viscosity, production of gases). Only some 10 species of bacteria pose danger to construction materials, paints and any other bulk containing water, for instance: *Aerobacter sp.*, *Bacillus sp.*, *Citrobacter sp.* or *Proteus sp.* [2]. Fungal growth can be easily seen as mould or biological sediment on the surface or on the walls of containers. Fungi constitute a very complex group of single and multicellular organisms that use cellulose and proteins as nutrients. They can inhabit both organic and inorganic surfaces (wood, masonry, aluminium, plastics, plants, dust *etc.*). Literature lists about 19 fungi species, most often found in contaminated coating materials *e.g. Alternaria sp.*, *Aspergillus niger*, *Cladosporium sp.*, *Penicillium sp.* or *Aureobasidium pullullans* [2]. Contamination may occur when contaminated surface is coated with paint or when

T a b l e 1. Optimal conditions necessary for growth of microorganisms (according to [1])

Bacteria	Fungi	Algae
no light necessary	no light necessary	light
slightly alkaline pH	slightly acidic pH	neutral pH
25—40 °C	20—35 °C	15—30 °C
nutrients (source of C, H, N)	nutrients (source of C, H, N)	CO_2
trace elements	trace elements	trace elements
oxygen (O_2 or inorganic)	oxygen (O_2 or inorganic)	oxygen (O_2 or inorganic)
water	water	water

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fungi spores find suitable conditions for growth on a coating. Fungi influence decorative and protective properties of coatings. Fungal growth leads to the cracks, loss of adhesion to the surface, splitting or erosion of painted surfaces [1]. Two mechanisms of biodeterioration of paints and coatings can be distinguished: when coating materials constitute a source of nutrients for microorganisms and when metabolites produced by microorganisms in the nutrition cycle (enzymes or chemical compounds *e.g.* organic acids) released to the environment cause degradation of coatings. In the latter case organic material present in dirt or dust is used by microorganisms as a carbon source and a coating system acts as a surface, necessary for bacterial, fungal or algal growth [3]. Very often additives used in coatings systems (rheology additives, pigment pastes, surfactants *etc.*) may migrate to the top of the coating and become a substrate for some type of microorganisms [1, 4]. Microorganisms have strong tendency to adsorb onto material surfaces. Once microorganisms are attached to the surface, a multistep process starts, leading to the formation of a complex, adhering microbial community defined as biofilm. This microbial colonization can drastically modify the corrosion behavior of a wide range of materials [4]. For many years heavy metals have been used to kill and stop growth of microorganisms — as inorganic salts or organic compounds (*e.g.* organic tin compounds) [5, 6]. Even small amounts of heavy metals have significant antimicrobial effect. Despite excellent antimicrobial and technological properties mercury and tin compounds have been withdrawn due to their toxicity for higher organisms. Silver and copper, on the contrary, possessing the same excellent antimicrobial properties, do not show any adverse effects for humans and animals [3].

In the recent years there has been a growing interest in silver as effective antimicrobial agent. This drive toward silver has been caused by many reasons. Some of them are: legislation rules ["Biocidal Product Directive" (BPD) 98/8/EC and its implementation into national legislation of EU member countries], requirements imposed on properties of biocides (low toxicity to humans and animals, low solubility in water, resistance to temperature and sunlight, long lasting performance) and increasing resistance of microorganisms to biocides [7—9]. Literature data and patent survey [10—14] show widening field of silver use — in medicine (in composites and other materials used for prostheses, in aseptic wound dressings *etc.*), in textile industry (impregnation of fabrics) [5], in dentistry, in cosmetic industry or in plastics industry (in various household goods *e.g.* breadboards or chopping boards). Many patents address the problems experienced when using silver and its preparations, like darkening of silver-containing products (*e.g.* paints), oxidation of silver or problems with effective dispersion of silver preparations [16—19]. Silver is also used in hygienic coatings [20].

Considering all available data we have decided to take up a study to evaluate antimicrobial effectiveness of silver preparations in waterborne dispersion paints. Commercial silver preparations in form of powder (on SiO_2 as a carrier), water solution or paste (Ag on TiO_2) were used. Preparations were added to a base paint recipe. Base paint was prepared according to recipe elaborated during a separate study. Examinations of this paint performed earlier let us expect that its components would not be a source of nutrients for microorganisms [21]. We have used two concentrations of silver — 30 or 40 ppm (by weight), taking into account data given in literature, concerning effective concentrations of silver in various uses. Coatings on glass, cardboard-plaster and lignin-cement plates were prepared, and divided into two parts — one was stored in a cool, dark, dry place and the other was exposed to accelerated ageing test.

EXPERIMENTAL

Materials

Commercially available acrylic binder (50 % dispersion in water characterized by minimum film formation temperature *MFFT* = 3 °C, pH = 8—10 and viscosity 50—200 mPa · s), pigment (TiO_2, rutile form), extenders (marble, micronized talc), additives (wetting and dispersing agents, defoamer and softening agent), acrylic thickener (50 % solution in water) were used to prepare the base paint. Four different commercially available preparations containing silver as an antimicrobial agent were added to the prepared base paint recipe to obtain paints F1—F4:

— solution of colloidal silver (ϕ = 40—50 nm) in water (1);

— solution of nanoparticles of silver in water (ϕ = 1—5 nm, concentration of 2 g/dm^3) (2);

— AgCl with TiO_2 and surfactant in form paste (3);

— powder of Ag, AgCl and TiO_2 (4).

Preparation of samples

Dispersion base paint (denoted F0) and paints containing silver preparations 1—4 in amount 30 ppm (recounted per Ag) (denoted F1/30 — F4/30, respectively) or 40 ppm (denoted F1/40 — F4/40, respectively) were

T a b l e 2. Components of base paint and silver containing paint

Components of paints	Concentration of component	base paint	paints with Ag
acrylic binder	10 wt. %	+	+
pigment	10 wt. %	+	+
extenders	55 wt. %	+	+
additives	1 wt. %	+	+
acrylic thickener	0.5 wt. %	+	+
silver preparation	30 ppm or 40 ppm	–	+
water	23.5 wt. %	+	+

prepared with high-energy mill (atritor) as 500 g samples. Table 2 presents the components of paints and their concentrations. Components chosen for the base paint should not be susceptible to microbial attack. Especially acrylic thickener used instead of more popular cellulose thickeners should prove helpful to reach that goal. During preparation of paints with silver we have found out that it was of a great importance to disperse silver preparation well, as any inaccuracy led to non-homogeneity of a composition and manifested as stains, cream to yellow colored, on the coating surface. For each paint the coatings on glass, cardboard-plaster and lignin-cement plates were prepared.

Methods of testing

Coatings were allowed to dry and were divided into two parts. One was stored in a cool, dark, dry place and the other was exposed to accelerated ageing test. Whiteness (W_e) and yellowness (Y_e) of coatings after the ageing test (according to PN-ISO 11507:2007) were measured with X Rite 968 (illuminant C^2) according to standard PN-72/C-81546.

Microbiological tests were performed with two methods, A and B respectively. Method A is used to estimate natural microbial resistance of a tested material. There are no additional nutrients except for those in material itself. Method A is used to examine if coating can serve as source of carbon for microorganisms and contribute to their growth. Examinations were carried out at 29 ^oC, at relative air humidity 80—90 %, for 30 days. Method B corresponds to natural conditions, when dirt, grease, dust and similar materials are deposited on the coating. This method tests fungistatic properties of a coating and influence of contaminants on its microbial resistance. Temperature, relative air humidity and time are the same as in Method A. Table 3 presents scale used to evaluate the intensity of growth of microorganisms on the glass surface, lignin-cement plates and on cardboard plates. 0 represents the minimum value (no growth) and 5 the maximum value (intensive growth on all the surface). Results of the evaluation were used to describe microbial resistance of tested coatings (Table 4).

T a b l e 3. Evaluation of microbial growth according to standard PN-85/C-89080

Intensity of growth	Scale
No growth visible under the microscope	0
Very slight growth seen only under the microscope, not visible with a naked eye	1
Visible growth, covering maximum 25 % of the surface, visible with a naked eye	2
Visible growth, covering maximum 50 % of the surface, visible with a naked eye	3
Significant growth covering more than 50 % of the surface	4
Intensive growth on all the surface	5

T a b l e 4. Evaluation of tested specimens according to standard PN-85/C-89080

Method	Intensity of growth	Evaluation of the specimen
A	0	material does not serve as nutrient for microorganisms
	1	material contains substances that serve as nutrients for microorganisms or is slightly contaminated and thus tiny microbial growth is possible
	2 to 5	material is susceptible to microbial attack and serves as nutrient for microorganisms
B	0	strong fungistatic effect
	0 + inhibition zone	strong fungistatic effect covering area surrounding the sample
	1 to 5	no fungistatic effect

RESULTS AND DISCUSSION

Tests with fresh coatings

First tests were performed on the glass plates and lignin-cement plates. Method A showed that the paints (their components) do not serve as sources of carbon for tested microorganisms (Table 5 and 6). Cardboard plates constitute a separate case. Growth of fungi on cardboard plates, covering in most cases 100 % of a surface, occurs because the components of cardboard plates (mainly cellulose) are very suitable surfaces for fungal growth. Such plentiful growth indicates at the same time that silver added to a paint is not sufficient to protect this type of surface and to prevent fungal growth. No influence of silver concentration on its antimicrobial efficiency was observed in method A for coatings on glass. Method B gave varied results depending on the type of surface (glass, cardboard plates or lignin-cement plates) and on the species used in tests (Table 7 and 8). F0 (a reference sample) was susceptible to microbial growth. Microorganisms colonized paint F0 with different intensity. A very intensive growth was observed for coatings on glass whereas growth on lignin-cement plates was far less intensive. To explain the difference in behavior observed for the same preparations on different surfaces, pH of water with immersed lignin-cement plates was measured. pH values were as high as 9—11 and this most probably influenced the growth of microorganisms in addition to silver activity. For coatings on glass plates the most intensive growth was observed for *Cladosporium cladosporioides* and *Penicillium chrysogenum* and for coatings on lignin-cement plates — for *Cladosporium cladosporioides* and *Aspergillus versicolor.* In these tests the differences of efficiency among silver preparations used in the paints were observed. *E.g.* there was greater effectiveness of preparation in paint F4/30 compared to preparation used in paint F1/30. Preparation used in paint F2/30 (coatings on glass surface) could only inhibit

T a b l e 5. The results of microbiological tests performed by method A for samples containing 30 ppm of silver in comparison with base paint

Strain	Intensity of growth (0 to 5 scale)									
	Glass surface					Lignin-cement plates				
	F0	F1/30	F2/30	F3/30	F4/30	F0	F1/30	F2/30	F3/30	F4/30
Aspergillus niger	0	0	0	1	0	0	0	0	0	0
Cladosporium cladosporioides	0	1	0	0	0	0	1	0	0	0
Aspergillus versicolor	1	0	0	0	0	0	0	0	0	0
Penicillium chrysogenum	0	0	0	0	0	0	0	0	0	0

T a b l e 6. The results of microbiological tests performed by method A for samples containing 40 ppm of silver in comparison with base paint

Strain	Intensity of growth (0 to 5 scale)							
	Glass surface				Cardboard plates			
	F0	F2/40	F3/40	F4/40	F0	F2/40	F3/40	F4/40
Aspergillus niger	0	0	0	0	5	5	5	3
Cladosporium cladosporioides	0	0	0/1	0	5	5	5	3
Aspergillus versicolor	0/1	0	0	0	5	4	5	5
Penicillium chrysogenum	0	0	0	0	5	5	5	5

T a b l e 7. The results of microbiological tests performed by method B for samples containing 30 ppm of silver in comparison with base paint

Strain	Intensity of growth (0 to 5 scale)									
	Glass surface					Lignin-cement plates				
	F0	F1/30	F2/30	F3/30	F4/30	F0	F1/30	F2/30	F3/30	F4/30
Aspergillus niger	3	2	1	0	0	2	1	0	0	0
Cladosporium cladosporioides	5	2	0	0	1	3	0	0	0	0
Aspergillus versicolor	3	1	1	1	1	3	1	0	0	0
Penicillium chrysogenum	5	4	1	0	0	2	0	0	0	0

growth of one of tested microorganisms — *Cladosporium cladosporioides*. However, it is noteworthy that the growth of *Aspergillus niger*, *Aspergillus versicolor* and *Penicillium chrysogenum* on paint F2/30 was less intensive in comparison to reference sample F0. Results obtained in Method B for lignin-cement plates were excellent as all preparations of silver could inhibit the growth of all microorganisms used in tests.

T a b l e 8. The results of microbiological tests performed by method B for samples containing 40 ppm of silver in comparison with base paint

Strain	Intensity of growth (0 to 5 scale)			
	Cardboard plates			
	F0	F2/40	F3/40	F4/40
Aspergillus niger	4	3	3	4
Cladosporium cladosporioides	5	4	4	4
Aspergillus versicolor	4	3	3	3
Penicillium chrysogenum	4	3	4	3

Tests with coatings after accelerated ageing

Tests of coatings (on glass, cardboard plates and lignin-cement plates) submitted to accelerated ageing were performed with method A and method B, respectively. Coatings on a glass (method A) gave the same results as in previous experiments — there was no growth of microorganisms on any of the coatings submitted to tests. However different observations were made for the coatings on cardboard plates, where growth of microorganisms was very intensive and in some cases almost 100 % of the surface was covered by moulds. Intensity of growth on specimen with and without silver was almost the same. Only for coatings F3/40 and F4/40 growth of *Aspergillus versicolor* was less intensive than on reference paint F0. *Penicillium chrysogenum* was the most resistant to silver and covered the biggest area of the coating (Table 9).

In method B silver proved to be the most effective (coatings on a glass) against *Cladosporium cladosporioides* and *Penicillium chrysogenum* (Table 10). The growth of

microorganisms on all coatings containing silver was reduced to the edges of specimens, there was no active mycelium, only discoloration was visible. In case of cardboard plates, when an easily accessible source of carbon was present (glucose added to the broth) the growth of microorganisms covered about 50 % to 100 % of the surface. Only for two specimens, *Cladosporium cladosporioides* and *Aspergillus versicolor*, the growth was smaller (paint F4/40) than on the reference sample F0. For paint F2/40 only growth of single specimen *Aspergillus versicolor* could be inhibited but not fully stopped.

T a b l e 9. The results of microbiological tests performed by method A on cardboard plates for samples incubated for 30 days

Strain	Intensity of growth (0 to 5 scale)			
	F0	F2/40	F3/40	F4/40
Aspergillus niger	4	5	4	5
Cladosporium cladosporioides	4	5	5	5
Aspergillus versicolor	5	5	4	3
Penicillium chrysogenum	5	5	5	5

T a b l e 10. The results of microbiological tests performed by method B on glass plates for samples incubated for 30 days

Strain	Intensity of growth (0 to 5 scale)		
	F0	F2/40	F3/40
Aspergillus niger	2	3	3
Cladosporium cladosporioides	2	1	1
Aspergillus versicolor	3	3	3
Penicillium chrysogenum	3	1	1

T a b l e 11. The results of microbiological tests performed by method B on lignin-cement plates for samples incubated for 30 days

Strain	Intensity of growth (0 to 5 scale)			
	F0	F1/30	F3/30	F4/30
Aspergillus niger	4	2	3	1
Cladosporium cladosporioides	5	5	5	5
Penicillium chrysogenum	5	2	4	3

In the next step method B was applied to coatings F0, F1/30, F3/30 and F4/30 on lignin-cement plates submitted to accelerated ageing in Q-panel (Table 11). Almost all surface of coating F0 was covered by moulds (all 4 species). Addition of silver preparation resulted in inhibition of growth of two moulds: *Aspergillus niger* and *Penicillium chrysogenum*. *Cladosporium cladosporioides* was the most resistant to silver. Its growth on coatings F1/30, F3/30 and F4/30 was the same as on reference coating F0. It is noteworthy that the growth of moulds on coatings was not too intensive, a slight discoloration was observed and there was a slight deposit of conidia. There was no active mycelium. Results of Y_e and W_e measurements presented in Table 12 indicate that, as a general rule, addition of silver does not influence whiteness of coatings. Only for paint F2 addition of silver preparation led to loss of W_e of circa 25 % in comparison to F0. In our opinion this behavior can be explained by instability of that particular silver preparation under UV light.

T a b l e 12. Results of whiteness (W_e) and yellowness (Y_e) measurements

Symbol of sample	Glass plate		Lignin-cement plate		Cardboard plate	
	W_e	Y_e	W_e	Y_e	W_e	Y_e
F2/40	53.90 53.37	8.64 8.72	— —	— —	58.35 59.88	7.86 7.34
F4/40	72.23 72.58	4.34 4.21	— —	— —	67.4 67.24	5.91 5.14
F3/40	72.28 72.71	3.86 4.14	— —	— —	67.1 66.95	5.58 5.78
F0	72.74 71.19	4.15 4.37	— —	— —	67.29 65.04	5.72 5.06
F1/30	70.28 70.19	3.44 3.34	69.81 70.36	5.02 4.51	— —	— —
F3/30	74.82 75.56	3.78 3.69	69.22 69.1	6.35 6.32	— —	— —
F4/30	72.04 70.81	5.7 5.59	66.87 66.69	7.69 7.27	— —	— —
F0/30	71.84 71.3	4.53 3.43	68.49 68.94	6.8 6.72	— —	— —

CONCLUSIONS

In the course of experiment we were able to obtain a recipe of stable dispersion paint for an interior use, containing silver and showing fungistatic action. This paint consists of the components that are not sources of nutrients for microorganisms which makes paint less susceptible to microbial attack.

Microbiological examinations proved that in tested paints silver acted as an antimicrobial agent, however it could only decrease the growth of moulds but not stop it completely. Effectiveness of silver was dependent upon type of coated surface (its pH value — as observed for lignin-cement plates, impurities, components that microorganisms can use as nutrients), the type of moulds that inhabit the coating and the type of a silver preparation.

Comparison of the results obtained for coatings on a glass surface, on lignin-cement plates and cardboard plates shows that different factors that influence fungistatic effectiveness of silver may contribute to improved fungistatic effect (*e.g.* high pH) or may lower fungistatic efficiency significantly (*e.g.* the presence of a cellulose in

the coated material as in cardboard plates used in experiments). Thus it may not be assumed that paint containing silver that proved effective in one application will produce the same or comparable results when applied to different surfaces.

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