NUKLEONIKA 2006;51(Supplement 1):S69–S72



# Silica materials with biocidal activity

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**Abstract** Pathogenic microorganisms like fungi, bacteria and algae are harmful to human beings and animals. Moreover, they contribute to the destruction of building materials by their biodegradation. Therefore, they create serious hazard for the natural environment. To prevent these phenomena, different materials with biocidal activity are being developed. In elaboration of such materials, one of the most difficult problems to be solved is the achievement of their high effectiveness in controlling harmful microorganism population with the guarantee of safety of their application to the natural environment and humans. As a result of investigation carried out in the INCT on new biocides based on quaternary *N*-alkylammonium salts (QAC), mainly benzalkonium chloride, and water glass (WG) large group of new silica materials with biocidal activity were synthesised. Possibilities of technology modification in order to obtain different profitable properties of materials are presented in the paper. Preliminary investigations concerning biocidal activity against selected mould fungi, bacteria and algae were performed. Results of microbiological investigations proved stable effectiveness of biocides for protection from harmful microorganisms growth, which does not decrease even after washing of biocidal material with water. Silica materials with biocidal activity due to structural binding of biocidal agent (QAC) can be applied in building industry as materials of high ecological safety.

**Key words** biocides • quaternary *N*-alkylammonium salts • silver metallized coatings

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Received: 2 November 2005

## Introduction

As a result of investigations carried out in the INCT on new biocides based on quaternary *N*-alkylammonium salts (QAC) and water glass (WG) group of new silica materials with biocidal activity were elaborated [2, 3]. Quaternary *N*-alkylammonium salts are known as cationic surface-active substances. They are commonly used in industry: in fabric production, cosmetology or as food preservatives. Biocidal agent in our material is benzalkonium chloride (Fig. 1), which is used as antiseptic, disinfectant, detergent and preservative [1]. Silica biocides are safe for the environment, because a biocidal agent is stably bound in the material and does not penetrate into the natural environment. Additional biocidal compounds like silver can be bound in the materials. Solid biocidal materials can be also incorporated into fabrics.

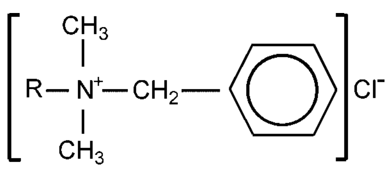


**Fig. 1.** Chemical formula of benzalkonium chloride.

Materials described in this paper were obtained by coating a carrier (C) (e.g. $TiO_2$, dolomite, bentonite etc.) with aqueous solution of sodium silicate salt (water glass) and compound QAC:

$$Si(ONa)_n(SW) + QAC^+Cl^- \rightarrow Si(ONa)_{n-1}QAC + NaCl$$
$$C + Si(ONa)_{n-1}QAC \rightarrow C[Si(ONa)_{n-1}QAC] \rightarrow C(SiO_2\text{-}QAC)$$

The material coated with sodium silicate salt and QAC is stabilised by $H_2SO_4$. Materials obtained according to our technology can be very well disperged in resins due to highly developed surface and their homogeneous structure. Preliminary assessments of the materials created by coating confirm their interesting biocidal properties.

An important advantage of the technology is the possibility of material modification by application of different kinds of carriers in different quantities in order to obtain specific, required properties.

## Experimental

### Materials

Sodium silicate (water glass) "STANDARD" (~ 40%), benzalkonium chloride (QAC) (Fluka or Bayer), $TiO_2$, colloidal silica Ludox (30%) (Du Pont).

### Methods

Aqueous solution of water glass (WG) and benzalkonium chloride (QAC) was prepared by addition of 20 ml of water glass to 10 ml of QAC (50%) and 30 ml $H_2O$. QAC/WG ratio can be also higher two times. Material C was coated with WG-QAC salt according to the following procedure: material C [10 g, $TiO_2$, dolomite, dolomite (90%) + $TiO_2$ (10%) or Ludox (10 or 20 ml)] was stirred with 30 ml of WG-QAC for 15 min, then ~ 70 ml of $H_2O$ was slowly added during continuous stirring. Gradually, coating of the product (or $SiO_2$ precipitated from Ludox solution) was achived. WG-QAC salt dissolves in water only in a strictly defined concentration range. After addition of water to the mixture, 10 ml of 18% $H_2SO_4$ was added and then it was stirred for about 10 min and left for 2 h. Obtained product $C(SiO_2\text{-}QAC)$, stabilised by sulphuric acid, was filtered off, washed with water and dried in air.

### Silver coatings. Methods

2 ml of 2% $AgNO_3$ was added to 0.4 g of $SiO_2(TiO_2)$-QAC and the sample was stirred for 10 min. After washing with water, the sample prepared in this way was irradiated with UV. Very fast change of the sample color (from white to dark brown) due to silver bound in the reduction material was observed.

Biocidal silica materials bind $Ag^+$ from aqueous solutions creating $SiO_2$-QAC]$Ag^+$ and $C(SiO_2$-QAC)]$Ag^+$ materials. These materials can be dispersed in resins. Different surfaces can be covered with the dispersion and, after UV irradiation, homogeneously colored coating with reduced silver was obtained. Very high effectiveness of $Ag^+$ fotochemical reduction, especially for materials containing $TiO_2$ as a carrier, was observed. Silver coatings can be applied for the preservation of different surfaces.

### Binding of biocidal silica materials in fabrics. Methods

A fabric was immersed in an aqueous solution of SW-QAC. After 2 h, the excess of SW-QAC from the impregnated fabric was removed and a small amount of $H_2SO_4$ (or other acid) was added. After 1–2 h, the sample was washed with water and dried in air.

Fabrics impregnated with biocidal material have stable properties (even after washing): affinity to acid dyes (e.g. Acid Green 27), ability of $Ag^+$ binding and silver fotochemical reduction. The fabrics prepared according to this technology can be applied as antibacterial filters, medical dressing or medical radioapplicators.

### SEM investigations

Preliminary SEM (scanning electron microscopy) investigations suggest that metallic silver create 30–50 nm nanoparticles on the biocidal material grains (Fig. 2). Three SEM images for non-modified biocidal material, biocidal material with silver coating and UV irradiation and the same material after $HNO_3$ treatment that caused silver coating dissolution, are presented in Fig. 2.

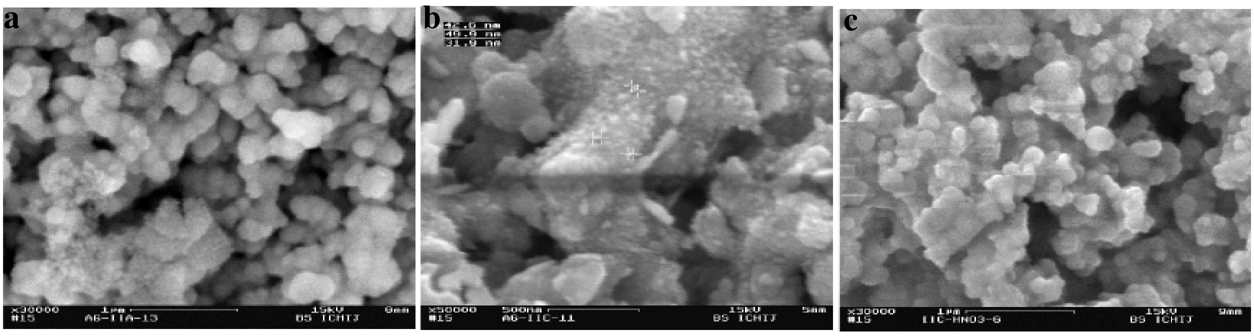


**Fig. 2.** SEM photomicrograph of $SiO_2(TiO_2)$-QAC material (a), $SiO_2(TiO_2)$-QAC material with silver coating after UV irradiation (b), $SiO_2(TiO_2)$-QAC material with silver coating after UV irradiation and $HNO_3$ treatment (c).

**Table 1.** Gradual scale according to which microbiological protection of the sample (level of fungi growth) was estimated

| Grade range | Effectiveness estimation |
|---|---|
| 0 | very high effectiveness |
| 0–1 | high effectiveness |
| 1–5 | no effectiveness |

**Table 2.** Estimation of growth of test fungi on samples

| | Result of growth of fungi estimation, stage of growth | | | | |
|---|---|---|---|---|---|
| Kind of the sample biocide addition [%] | Set I without elution | Set II without elution | Set III without elution | Set II with elution | Set III with elution |
| White gypsum, without biocide | 3–5 | 5 | 4 | 5 | 4 |
| White gypsum, 1% biocide | 1–2 | 1 | 1 | 1 | 1 |
| White gypsum, 1.5% biocide | 0–1 | 0 | 1 | 0 | 1 |
| White gypsum, 2% biocide | 0–1 | 0 | 1 | 0 | 1 |
| White gypsum, 2.5% biocide | no data | 0 | 1 | 0 | 1 |
| White gypsum, 3% biocide | 0–1 | 0 | 0 | 0 | 0 |

It is probable that silver creates grains of tens of nanometers in size on the material surface (Fig. 2b).

### Microbiological investigations

Round plates of white gypsum, 25 mm diameter and 3 mm thickness, were used in investigations of the material biocidal activity against mould fungi. Such samples were preserved with addition of 1, 1.5, 2, 2.5 and 3% of the biocide. Samples without addition of the biocidal material were used as a control. After their preparation, the samples had been seasoned 28 days. Sets of 12 plates, each sample with different concentration of biocide in gypsum and each sample for different set of fungi were used in biological investigations. Six samples were subjected to fungi without elution with water and another six were washed with water before their exposition to fungi according to the PN-EN 84 standard. The samples were placed directly on the agar base and were inoculated with spore suspension of test fungi. The following fungi were used in biocidal activity investigations:

Set I: *Mucor piriformis* Fischer;
Set II: *Chaetomium globosum* Kunze;
Set III: (different kinds of fungi): *Aspergillus niger* van Tieghem, *Aspergillus terreus* Thom, *Paecilomyces variotii* Bainier, *Penicillium funiculosum* (Thom), *Penicillium ochrochloron* (Biourge), *Scopulariopsis brevicaulis* (Saccardo) Bainier, *Trichoderma viride* (Pers. ex Fries).

Perti dishes with a diameter of 180 mm with agar base were applied for incubation for 28 days at 26 ± 1°C and at an air relative humidity of 90–95%. Each sample of each microbiological protection variant together with control sample were placed in a separate vessel. After exposition, the samples were inspected visually according to the gradual scale (Table 1).

Total effectiveness was estimated as an average from the inspection of all samples of one kind.

Results of biocidal activity of the material against mould fungi are presented in Table 2. Taking into account the results, we can state that all sets of test fungi are sensitive to even small additions of the biocidal material to the sample. Results are satisfactory for the samples with added biocidal material above 1.5%. Fast growth of mould fungi on control samples (without biocidal material addition) was observed [4].

## Conclusions

- Material obtained by coating of QAC shows stable effectiveness in protection of material from fungi and bacteria growth.
- Effectiveness of the biocidal material activity does not decrease even after preliminary treatment of the material with water (no removed by wash).
- Material binds silver, which creates nanoparticles of 30–50 nm in size on biocidal material surface, from water solutions. It enhances biocidal effect and gives the possibility for multiple material applications as well.
- Potential application of the biocidal materials are building industry (as additives to paints, mortals etc.), medicine (as antibacterial filters, medical dressing or medical radioapplicators) and as an agent for the decontamination of different surfaces.

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