BIOCIDAL METALLIC GLAZES FOR PORCELAIN FLOOR TILES

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The urgency of obtaining of antibacterial glaze coatings for floor tiles relates to the lack of efficiency of the known ways to prevent the reproduction of pathogenic bacteria. As is known, copper and some of its alloys are characterized by pronounced biological activity. Antibacterial properties of copper compounds are used in the manufacture of medicine equipment, in food industry and animal husbandry [1], and to provide antifungal and antimicrobial properties of sanitary ceramics, ceramic tiles [2]. The aim of this work was to study the formation of the glaze coatings for ceramic porcelain tiles with the required physico-mechanical properties and aesthetic characteristics, as well as reliable antibacterial protection.

The glaze slip was prepared by combined wet grinding of the components of the glaze batch in a ball mill (Speedy, Italy) to 0.1–0.3 wt. % residue in a No. 0056 sieve with material : milling body : water ratio 1 : 1.5 : 0.5. Sodium tripolyphosphate in the amount of 0.25 wt. % over 100 % was used as the deflocculant. The suspension obtained with moisture content 30–40 wt. % was deposited on ceramic porcelain tiles predried to moisture content no more than 0.5 wt. % and coated with engobe. The tiles glazed with the experimental glaze compositions were fired in an FMS-2500 gas-flame furnace (Sacmi, Italy) at temperature (1200±5) ºC for (50±2) min under the extant conditions at Keramin JSC (Minsk, Republic of Belarus).

Physical-chemical properties of glaze samples after synthesis were tested for conformity with the requirements of technical standards documents. The antimicrobial activity tests of the glaze coatings were conducted in the laboratory of microbiology of RUE "Scientific and practical center of hygiene" (Minsk, Republic of Belarus). The laboratory is accredited in the field of determination of antibacterial activity on ceramic surfaces, including tiles in accordance with ISO 22196: 2011. The oxide compositions of the experimental glazes are given in table 1.

Table 1 – The oxide compositions of the experimental glazes

Oxide	**Oxide ratios of the glazes of the series, wt. %**		
	1	**2**	**3**
SiO_2	37–44	38–44	35–41
Al_2O_3	15–17	21–23	13–15
(CaO + MgO)	15–23	11–13	17–23
(Na_2O + K_2O)	5–6	6–8	5–6
CuO	11–22	12–22	10–19
B_2O_3	1–2	1–2	1–2
Fe_2O_3	–	–	5–7

The study of physical-chemical properties founded that, synthesized glaze coatings conformed to requirements of technical standards documents, as well as had high

decorative effect (table 2). In addition, all glaze coatings were chemically stable. Furthermore, antibacterial activity tests of glaze coatings by using were carried out with the test strain Escherichia coli ATCC 8739 and Staphylococcus aureus ATCC 6538 (table 2).

Table 2 – Physical-chemical and antimicrobial properties

Description	The glazes of the series		
	1	2	3
Color	Black	Dark grey	Dark grey
Surface texture	Semi-matte, lustrous	Matte	Matte, semi-matte, lustrous
Luster, %	45–100	16–31	5–100
Microhardness, MPa	3900–6100	5100–6800	5800–7800
The linear thermal expansion coefficient, $\alpha \cdot 10^{-7}, K^{-1}$	84.9–89.5	67.9–74.6	58.7–72.1
Heat resistance, °C	100–200	150–200	125–150
Class of surface abrasion resistance	1	2	1–2
The value of antibacterial activity	2.56–2.89	0.64	2.00–2.17

The XRD patterns of the glazes of the series 1 showed tenorite (CuO) and anortite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). However, the presence of the amorphous halo in the X-ray diffraction patterns, along with broad and low intensity crystalline peaks indicated that the coatings contained predominately glassy phase. Glassy phase was also predominantly in the glazes coatings of the series 3, small amounts of tenorite and maghemite (γ-Fe_2O_3) were also detected. The following crystalline phases were identified in the glazes of the series 2: tenorite, anorthite and cuprite (Cu_2O). In contrast to the glazes of the series 1 and 3 there was almost no the amorphous halo on the XRD patterns of the glazes of the series 2.

In our research biocidal glaze compositions for porcelain floor tiles were developed. The use of ceramic tiles decorated with elaborated compositions of glaze compositions will provide reliable antibacterial protection against strains of Staphylococcus aureus ATCC 6538 and Escherichia coli ATCC 8739. The tests performed under production plant conditions at Keramin JSC (Minsk, Republic of Belarus) showed that the newly developed coatings can be used in industrial manufacturing.

References

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