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Chemical resistance and cleaning properties of coated glazed surfaces

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Abstract

The effects of sol–gel-derived ceramic titania and zirconia coatings on staining resistance and cleanability of two matt and one glossy glazed tile were characterized. The surfaces were soaked in a weakly alkaline detergent solution in order to imitate the influence of normal household detergents on the surface properties. The soaking caused the water contact angle of the surfaces to decrease and also changes were observed in the average surface roughness. The surfaces were soiled with one color marked and two radiochemically labeled soil mixtures of oils and inorganic or organic particles. Under normal laboratory illumination conditions, the soils consisting of oil and inorganic particles were more easily cleaned from the surfaces than the soil with oil and organic particles. All surfaces soiled with the color marked mixture were also studied under exposure to UV light. The titania coating increased the cleanability and also showed self-cleaning capability after exposure to UV light, whereas exposure to UV increased the soil adherence to the zirconia-coated surfaces.

Keywords: A. Films; C. Corrosion; D. Glass-ceramics

1. Introduction

One of the main purposes of functional coatings on materials used in everyday life is to provide the surface with self-cleaning properties. When used, for example, on outdoor surfaces, the cleaning occurs through the interaction between UV-radiation and rain. The most common methods to characterize the activities of photocatalytic coatings on commercial products were discussed recently by Mills and McFarlane.[1] The activity of self-cleaning titania photocatalytic coatings on glasses is usually studied using the stearic acid test. The methylene blue test is also frequently used for assessing the photocatalytic activity of titania.[1] Examining the destruction rates of stearic acid and methylene blue under defined conditions is well suited to comparing the self-cleaning effectiveness of different surfaces; however, this requires sophisticated analytical equipment.[1]

On interior surfaces of buildings, various types of cleaning methods are needed for their maintenance. Cleanability of interior surfaces has been studied by soiling them using materials containing radioactive tracers or staining compounds. Radiochemically labeled soils permit accurate measurements at very low levels of soil. These soils have been used to measure the cleanability of plastic and ceramic surfaces.[2–5] Staining or cleanability of plastic and ceramic surfaces has also been studied colormetrically.[6–9] The soiling compounds applied in cleanability studies of glazed and titania-coated surfaces include, e.g. glycerol trioleate, octadecane, stearic acid, standard red soil, acetic acid, sebum soil and oleic acid.[7–15]

The main functions of additional coatings on interior surfaces include increased cleaning intervals and an increased possibility to use less aggressive cleaners. The chemical resistance of functional coatings on glazed surfaces has been reported to depend strongly on the phase composition of the glaze.[16] Commercial easy-to-clean fluoropolymer coatings (ECC-100 and ECC-400 by 3M) were found to degrade rapidly in alkaline environments.[15] In alkaline aqueous solutions, the same sol–gel-derived titania and zirconia coatings as reported in this work were found to be severely pitted on glazes containing wollastonite or pseudowollastonite crystals, i.e. on glazes which have poor chemical resistance.[16,17] However, on glazes showing a good overall chemical resistance the additional coatings were found to be fairly intact.[16,18]

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This paper is the third in a series in which the effect of additional sol–gel-derived titania and zirconia coatings on glazes is discussed.[4,5] In the previous papers, the cleanability of glazes with functional coatings was discussed. The focus of this paper is to establish whether a typical everyday detergent impairs the additional value of the coatings, i.e. their self-cleaning or easy-to-clean effects. One further goal is also to find a practical combination of soil and cleaning methods for easy comparisons of surface cleanability.

2. Experimental

Two commercial glazes and one experimental raw glaze were used as substrate materials for the additional coatings. The commercial matt (M) and glossy (K) glazes contained mainly zircon crystals embedded in the glassy phase on the surfaces. The experimental matt raw glaze (3A) contained mainly diopside crystals.[19] The glazes were dip coated with experimental sol–gel-derived titania and zirconia coatings.[20] The titania coating was assumed to enhance the cleanability of the surfaces. The zirconia coating was studied for establishing the possibilities of adjusting the properties of titania coatings by introducing some zirconia in order to improve chemical and mechanical properties.

Chemical wearing of the surfaces was achieved by soaking both coated and uncoated surfaces in a weakly alkaline detergent solution (pH 9.1) corresponding to a typical household detergent. The detergent consisted of soap (5%), non-ionic surfactant C13-oxoalcohol ethoxylate (10%) and tetrapotassium pyrophosphate (5%). Samples of 2.0 cm × 2.0 cm × 0.5 cm with 20 ml of detergent solution were put in covered containers and kept in a water bath at 37 °C for 4 days. The solution was replaced with fresh solution after 2 days. After soaking, the samples were rinsed carefully with distilled water and ethanol.

The surfaces were characterized by measuring the average surface roughness (S_a) with a white light confocal microscope (Nanofocus μSurf) before and after soaking. The roughness values were measured with a 20× lens for 772 μm × 800 μm surfaces (cut-off wavelength 250 μm). The static water contact angle was imaged for a water drop (ultra-pure Milli-Q) for 10 s, collecting one image per second using a contact angle meter (KSV CAM100). The contact angle, given as the mean of four parallel samples, was calculated with the Young–Laplace equation. The overall appearance and composition of the samples were also studied by FEG-SEM/EDXA (SEM, LEO 1530 from Zeiss, EDXA Vantage by Thermo Electron Corporation).

Cleanability of the surfaces was measured by color marked and radiochemically labeled mixtures of fatty acids and particles (Table 1). The soils with the radioactive tracers were assumed to be suitable for measuring the cleanability of rough tile surfaces as the soil which has penetrated into cracks and cavities is taken into account in the total soil amount. The color marked soil was used to allow a large number of measurements under normal laboratory conditions.

Soil 1 contained sebum, a typical fatty acid found in sanitary facilities. Sebum was mixed with fine soot particles of cosmetic quality in order to enable a colorimetric detection of the soil mixture on surfaces.[21] The components were thoroughly mixed with ethanol to a suspension which could be applied easily to surfaces by spin-coating. The soil suspension was stable and only a minor segregation of the components could be detected after mixing. Soil 2 consisted of chromium oxide and triolein. The inorganic Cr_2O_3 particles ($\varnothing = 1\ \mu m$) were labeled with ^{51}Cr. Soil 3 contained only organic components, i.e. particles of chromium acetyl acetonate labeled with ^{51}Cr and triolein. The components of soils 2 and 3 were dissolved in 1-propanol. Soil mixtures 2 and 3 did not form stable suspensions and some degree of segregation was observed after mixing.

Soil 1 was applied by spin-coating 20 μl of suspension four times on each surface. Before soiling, the surfaces were exposed to UV light (360 nm) for 2 h. The soil was dried for 24 h at room temperature and then re-exposed to UV light for 2 h before cleaning. The surfaces were cleaned with a microfiber-cloth moisten to 100% with distilled water in a Mini Cleanability tester. The microfiber cloth was rotated once against the surface with a pressure of 50 kPa and a velocity of 30 rpm. This cleaning step was designed to imitate a normal cleaning of interior surfaces. However, the parameters used for the Mini Cleanability tester were chosen to give only a partial cleaning with constant conditions so that clear differences between different surfaces could be established. The soil amount attached to the surfaces before cleaning, ΔE_s and the soil residue on the surfaces after cleaning, ΔE_{res} were calculated from the *CIE* $L^*a^*b^*$ values for the unsoiled, soiled and cleaned surfaces[6]:

$$\Delta E_s = \sqrt{(L^*_{unsoiled} - L^*_{soiled})^2 + (a^*_{unsoiled} - a^*_{soiled})^2 + (b^*_{unsoiled} - b^*_{soiled})^2}$$

$$\Delta E_{res} = \sqrt{\left(L^*_{unsoiled} - L^*_{cleaned}\right)^2 + \left(a^*_{unsoiled} - a^*_{cleaned}\right)^2 + \left(b^*_{unsoiled} - b^*_{cleaned}\right)^2}$$

In the equations, L^* is the lightness factor, a^* and b^* are the chromaticity coordinates giving the red to green and yellow to

Table 1
Compositions and amount of model soils applied on surfaces.

	Type of model soil	Particle compound	Solvent	Fatty acid	Radio isotope	Amount of soil
1	Inorganic particle and oil soil	Soot (Degussa AG) 0.050 g	Ethanol 0.50 ml	Synthetic sebum (WFK) 0.20 g	–	80
2	Inorganic particle and oil soil	Chromium(III) oxide, (J.T. Baker) 0.40 g	1-Propanol 10.0 ml	Triolein, (Fluka) 0.60 ml	^{51}Cr	50
3	Organic particle and oil soil	Chromium acetyl acetonate (Fluka) 0.40 g	1-Propanol 10.0 ml	Triolein (Fluka) 0.60 ml	^{51}Cr	50

blue hues of the color. The soil residue was also expressed as the ratio between the soil residue after cleaning and the amount of soil on the surfaces after soiling:

$$\text{Soil residue}\,(\%) = \frac{\Delta E_{res}}{\Delta E_s} \times 100$$

The radioactive soils were applied by pipetting the fluid soil (50 μl) onto the middle of the sample. The soil was left to dry for 24 ± 2 h at room temperature. The surfaces were cleaned with a microfiber-cloth moisten to 100% with distilled water containing 5 vol.% weakly alkaline model detergent in the Mini Cleanability tester.[3–5] The microfiber cloth was rotated three times against the surface with a pressure of 25 kPa and a velocity of 30 rpm.

The cleanability of the model soils labeled with the gamma-ray emitter ^{51}Cr was determined by a gammaspectrometric method using an NaI(Tl)-scintillation crystal as described in the first paper in this series.[4] The radioactivity of the soiled samples was measured before and after cleaning. The results were calculated by subtracting the activity of the background and correcting the results for radioactive decay. The soil residue (%) was calculated as the ratio between the soil residue after cleaning and the amount of soil on the surfaces after soiling.

3. Results and discussion

3.1. Chemical resistance of coatings

Chemical resistance of the additional coatings was studied from the water contact angle and surface roughness values before and after soaking the samples in the slightly alkaline detergent solution (Table 2). When the additional coatings were applied to the matt glazes (M and 3A), the contact angle clearly increased, while the value was quite stable for the coated glossy glaze K. Before soaking the contact angle values for the reference glazed surfaces were around 30–40°, i.e. typical values reported for silica and soda-lime glasses.[22,23] The contact angles of the titania-coated surfaces were 34–46°, depending on the substrate. Water contact angles of around 50° have been reported for smooth titania wafers irradiated with visible light.[24] The contact angle of the sol–gel-derived ZrO_2 showed the highest values for all surfaces, but the increase could be detected best with the matt surfaces. At 37–64°, the values were clearly lower than the value of ca. 100° reported for pure zirconia.[22] After 2 h of exposure to UV radiation, the contact angle of the TiO_2 surfaces decreased to below 10° (Table 2). The decline was so significant that the contact angle was not always measurable. UV light exposure also affected the water contact angles of the zirconia-coated surfaces (Table 2). However, the values were typical for ceramic surfaces and indicated no clear changes in surface wettability. Soaking the surfaces in the alkaline solution decreased the contact angle of all but the glossy glaze with the titania coating (Table 2). After exposure to UV light the TiO_2-coated surfaces showed similar contact angle values both before and after soaking. The results suggested that the titania and zirconia coatings were not attacked by the weakly alkaline cleaning agent solution.

Table 2
Contact angle and average surface roughness S_a of the experimental surfaces. Each value is an average of 4–10 parallel samples.

Surface	Contact angle (°)	Contact angle after UV (°)	Roughness (μm)
3A	33 ± 7.2	25 ± 6.1	0.41 ± 0.038
3A soaked	16 ± 4.2	12 ± 4.7	0.53 ± 0.074
3A + TiO_2	45 ± 6.4	9.0 ± 3.2	0.54 ± 0.022
3A + TiO_2 soaked	38 ± 6.4	6.0 ± 3.7	0.69 ± 0.034
3A + ZrO_2	64 ± 15	40 ± 7.5	0.48 ± 0.038
3A + ZrO_2 soaked	43 ± 7.2	37 ± 10	0.42 ± 0.057
M	31 ± 4.2	29 ± 4.9	0.39 ± 0.043
M soaked	19 ± 8.6	16 ± 5.6	0.39 ± 0.044
M + TiO_2	46 ± 3.4	7.0 ± 4.5	0.39 ± 0.011
M + TiO_2 soaked	36 ± 6.6	5.0 ± 2.5	0.43 ± 0.020
M + ZrO_2	61 ± 10	33 ± 6.8	0.35 ± 0.011
M + ZrO_2 soaked	47 ± 9.3	50 ± 7.1	0.36 ± 0.020
K	36 ± 7.4	29 ± 5.3	0.08 ± 0.01
K soaked	21 ± 7.6	22 ± 8.6	0.08 ± 0.01
K + TiO_2	34 ± 2.4	6.0 ± 4.3	0.09 ± 0.004
K + TiO_2 soaked	43 ± 10	5.0 ± 3.3	0.09 ± 0.004
K + ZrO_2	37 ± 2.1	40 ± 5.4	0.08 ± 0.003
K + ZrO_2 soaked	33 ± 3.4	46 ± 2.0	0.08 ± 0.004

The commercial matt and glossy glazes had a good chemical resistance as indicated by the average surface roughness values before and after soaking in the alkaline solution (Table 2). However, the soaking clearly increased the average surface roughness of the experimental matt glaze, thus implying selective corrosion of either the glassy or crystalline phase. The glaze with diopside crystals is reported to have a good chemical resistance in alkaline solutions.[25] Corrosion of some residual wollastonite could explain the observed change in surfaces roughness. However, neither the presence of wollastonite nor the corrosion could be verified from the SEM images.

The titania and zirconia coatings had negligible influence on the average surface roughness of the commercial and matt glossy glazes (Table 2). The coatings increased the roughness of the experimental matt glaze. The changes in the roughness values were assumed to depend mainly on cracks in the sol–gel-derived coatings. Fig. 1 shows an SEM image of a small crack on the titania-coated glaze 3A. After soaking in the weakly alkaline detergent solution wide cracks in the coating were observed (Fig. 2). The cracks were assumed to form mainly due to variations in the thickness of the coating and differences in thermal expansion of the coating and the substrate. However, crack formation can be avoided by a careful optimization of the parameters during the coating application and sintering.

3.2. Cleaning properties

The amount of soil that attaches to a surface before any cleaning is done can be used to estimate the soiling tendency of the surfaces. The total amount of soil 1 attached to the titania-coated surfaces before cleaning is shown in Figs. 3–5 as the whole bars for the soil residue and soil removed. As the commercial matt glaze (Fig. 4) and glossy glaze (Fig. 5) contained zircon

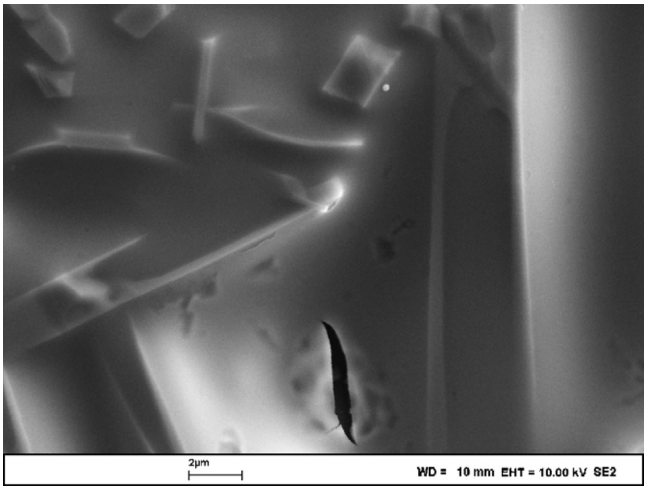

Fig. 1. SEM image of TiO_2-coated experimental surface (3A + TiO_2).

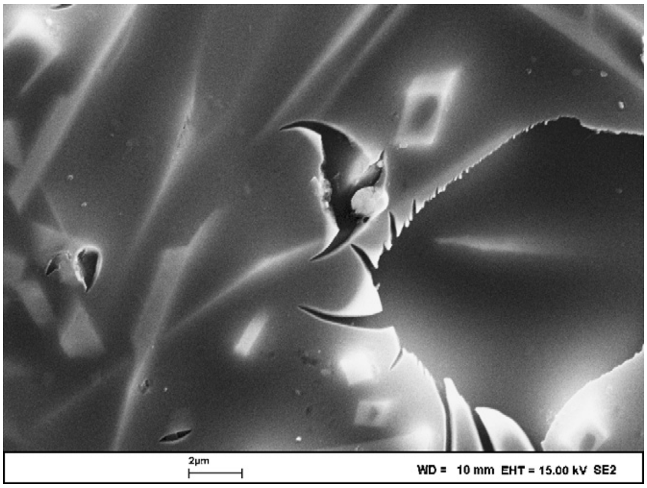

Fig. 2. SEM image of TiO_2-coated experimental surface (3A + TiO_2) after 4 days in weakly alkaline detergent solution (pH 9.1).

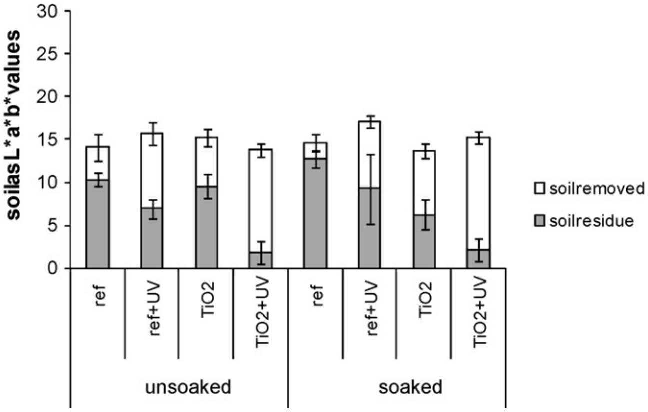

Fig. 3. Influence of soaking and UV exposure on total amount of soil 1 attached to uncoated and titania-coated matt 3A surfaces. The soil amount (ΔE_s) is given as the whole bar for soil residue (ΔE_{res}) and soil removed.

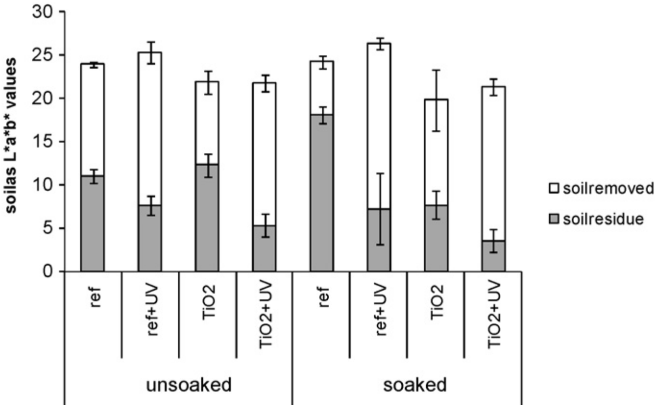

Fig. 4. Influence of soaking and UV exposure on total amount of soil 1 attached to uncoated and titania-coated matt M surfaces. The soil amount (ΔE_s) is given as the whole bar for soil residue (ΔE_{res}) and soil removed.

as the opacifying agent, the soot-colored soil gave a larger relative color change on them than on the experimental matt glaze without zircon (Fig. 3). After the soaking and UV steps, the relative amount of soil on each surface was still roughly the same as on the untreated reference glazes. On the titania-coated UV-exposed surfaces slightly less soil was observed.

A clear decrease in the soil residue was observed on the UV-exposed matt titania-coated glazes (Figs. 3 and 4). However, on the glossy glaze the soil residue value was low also on the reference-uncoated surface (Fig. 5). This could be explained by the overall easier cleanability of glossy surfaces. The results indicate that the titania coating clearly increased the cleanability of matt glazes, while on glossy surfaces the cleanability was good also without the additional coating.

Exposure to UV light clearly improved the cleanability of the titania-coated matt surfaces, but on uncoated samples the soil amount also decreased with the exposure to UV. The increased cleanability can partly be explained by some decomposition of the soil during the UV exposure due to an increase of 3 °C in the average surface temperature. The influence of irradiation time with UV light (360 nm) on soil degradation was studied

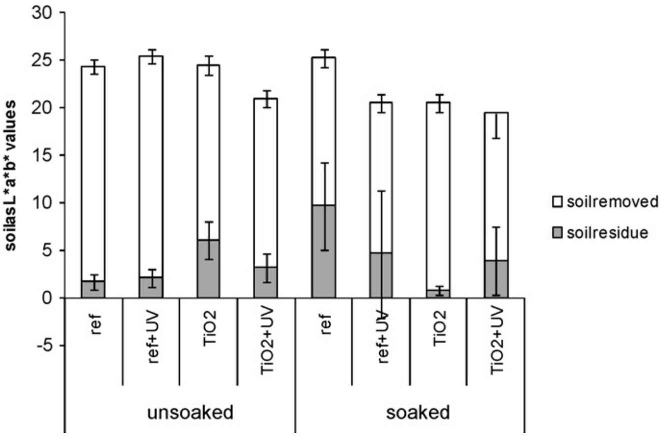

Fig. 5. Influence of soaking and UV exposure on total amount of soil 1 attached to uncoated and titania-coated glossy K surfaces. The soil amount (ΔE_s) is given as the whole bar for soil residue (ΔE_{res}) and soil removed.

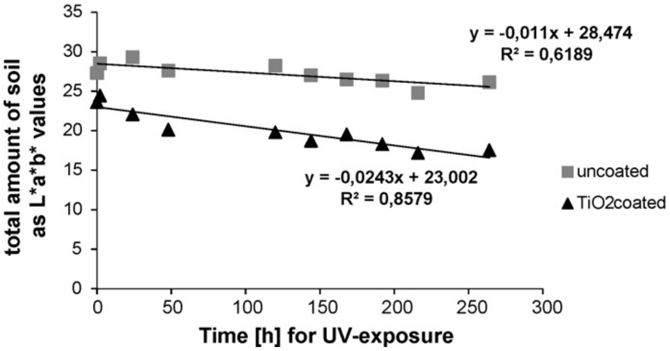

Fig. 6. Variation of the total amount of soil 1 attached to uncoated and titania-coated matt M surfaces vs. irradiation time (λ = 360 nm).

using the matt glaze M with and without the titania coating. The surfaces were first exposed to UV light for 2 h and then coated with soil 1. After drying for 24 h, the surfaces were placed under the UV-lamp and the amount of soil was measured for 264 h (Fig. 6). On both surfaces, a steady degradation of the soil was observed. On the titania-coated surface the original amount of soil attached to the surface was lower than on the uncoated surface. However, both surfaces were clearly discolored by the soil. The contact angles had different values, 5° for the titania and 29° for the uncoated surface. The soil decrease rate on the titania-coated surface was around twice that of the uncoated surface. This increased degradation rate of the soil on the titania coating can be explained by its photocatalytic activity.

Table 3 gives the soil residue (%) of the three soils on the surfaces after soaking. The residue of the soot-colored soil 1 was 50–90% on the matt uncoated and coated surfaces, while on the glossy-uncoated and titania-coated surfaces clearly lower soil residues, 7–25% were observed. The surfaces soaked in the weakly alkaline detergent solution showed slightly increased soil residues for all but the titania-coated surfaces. After the surfaces were exposed to UV light, the average value was lower on the titania-coated surfaces. Only on the corroded titania-coated glossy glaze was a slightly higher soil residue observed. The values clearly increased for all zirconia-coated surfaces exposed to UV light. Thus, different responses to soil removal were recorded for the titania- and zirconia-coated surfaces.

Table 3
Soil residue on the surfaces after cleaning. Each value is an average of 4–10 parallel samples.

Surface	Soil residue (%)			
	Soil 1	Soil 1 + UV	Soil 2	Soil 3
3A	73 ± 1.2	44 ± 1.2	4.3 ± 1.1	40 ± 12
3A soaked	87 ± 1.0	53 ± 2.4	6.9 ± 1.5	13 ± 1.0
3A + TiO_2	63 ± 1.2	13 ± 1.1	5.4 ± 0.19	35 ± 3.5
3A + TiO_2 soaked	46 ± 1.3	14 ± 1.0	3.8 ± 0.30	42 ± 4.9
3A + ZrO_2	75 ± 2.3	88 ± 1.6	4.0 ± 0.31	24 ± 5.1
3A + ZrO_2 soaked	75 ± 2.8	90 ± 1.7	6.1 ± 0.77	57 ± 13
M	46 ± 2.5	30 ± 2.4	4.6 ± 0.82	46 ± 7.0
M soaked	75 ± 1.1	28 ± 1.0	8.0 ± 1.00	17 ± 1.1
M + TiO_2	56 ± 1.2	24 ± 1.6	7.1 ± 0.40	34 ± 2.3
M + TiO_2 soaked	39 ± 4.0	17 ± 2.0	4.2 ± 0.32	37 ± 1.5
M + ZrO_2	69 ± 3.1	74 ± 1.2	5.4 ± 1.2	28 ± 3.3
M + ZrO_2 soaked	79 ± 3.7	97 ± 1.0	8.1 ± 1.2	50 ± 11
K	7 ± 0.8	8 ± 0.8	11 ± 1.0	62 ± 14
K soaked	36 ± 2.8	18 ± 3.5	15 ± 1.2	26 ± 14
K + TiO_2	25 ± 1.1	15 ± 1.2	8.2 ± 0.51	44 ± 3.9
K + TiO_2 soaked	4 ± 0.7	20 ± 3.1	7.0 ± 1.0	43 ± 2.8
K + ZrO_2	58 ± 2.0	65 ± 2.3	10 ± 0.93	28 ± 3.3
K + ZrO_2 soaked	79 ± 2.1	89 ± 1.6	14 ± 2.0	50 ± 11

The residue of soil 2, the suspension of Cr_2O_3 labeled with ^{51}Cr and triolein was low. The cleanability of the surfaces was measured under normal laboratory illumination conditions only. The soil residue was slightly higher on the smoothest surfaces, i.e. surfaces with the glossy glaze K as substrate, than on the matt glazes (Table 3). Slightly lower soil residue levels were observed on the titania-coated surfaces after soaking in the alkaline solution. On all other surfaces, somewhat higher soil residues were observed after the soaking.

The third soil, the suspension of organic particles labeled with ^{51}Cr in oil, showed clearly higher soil residues than the two other soils (Table 3). On all three glazes, the coatings improved the cleanability. The soil residue on the corroded-coated surfaces increased while the soil residue on the corroded reference surface decreased.

The soil residue values in Table 3 can be used to describe the relative cleanability of the surfaces after application of the different soils. The oil soil 1 marked with inorganic soot particles and the oil soil 2 with radiochemically labeled inorganic chromium oxide particles showed rather similar results. Thus, no essential differences were found between the adherences of these soil mixtures of inorganic particles and fatty acids to the surfaces. The soil consisting of triolein and organic particles more strongly adhered to the surfaces than the soil consisting of triolein and inorganic particles in accordance with earlier studies.[3,4] The two methods used to detect the amount of soil gave similar trends with comparable accuracy. However, the color marked oil soil was easy to prepare and required neither special equipment nor consideration of special laboratory safety regulations. Radiochemical determination provides information on the amount of soil both on the surface and penetrated into the material. However, the method can be used only in isotope laboratory conditions.

4. Conclusions

Sol–gel-derived ceramic titania and zirconia coatings on two matt and one glossy glaze slightly changed the overall roughness of the surfaces. The coatings had a good chemical resistance in normal household weakly alkaline detergent solutions. The sol–gel-derived ceramic titania coating clearly increased the cleanability of matt glazed surfaces, while its effect on the glossy glaze was not as pronounced. The coating also showed self-cleaning properties when exposed to UV light. The ceramic zirconia coating, however, was found to increase soil adherence to the surfaces. These results suggest that adjusting the properties of titania coatings by, for example, introducing some zirconia in order to increase mechanical resistance might adversely affect the self-cleaning capability of the coating.

The soil residue values suggested that the organic particle soil more strongly adhered to the surfaces than the oily particle soils. In principle, the soil residue values based on the color marked soil and the radiochemically labeled soils were comparable and of equal accuracy. However, the color marked soil can be easily measured with simple laboratory equipment, making it suitable for, e.g. easily comparing the self-cleaning capability of different surfaces.

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References

1. Mills, A. and McFarlane, M., Current and possible future methods of assessing the activities of photocatalyst films. *Catal. Today*, 2007, **129**, 22–28.
2. Pesonen-Leinonen, E., Redsven, I., Neuvonen, P., Hurme, K.-R., Pääkkö, M., Koponen, H.-K. *et al.*, Determination of soil adhesion to plastic surfaces using a radioactive tracer. *Appl. Radiat. Isotopes*, 2006, **64**(2), 163–169.
3. Määttä, J., Koponen, H.-K., Kuisma, R., Kymäläinen, H.-R., Pesonen-Leinonen, E., Uusi-Rauva, A. *et al.*, Effect of plasticizer and surface topography on the cleanability of plasticized PVC materials. *Appl. Surf. Sci.*, 2007, **253**(11), 5003–5010.
4. Määttä, J., Piispanen, M., Kuisma, R., Kymäläinen, H.-R., Uusi-Rauva, A., Hurme, K.-R. *et al.*, Effect of coating on cleanability of glazes surfaces. *J. Eur. Ceram. Soc.*, 2007, **27**, 4555–4560.
5. Määttä, J., Piispanen, M., Kymäläinen, H.-R., Uusi-Rauva, A., Hurme, K.-R., Areva, S. *et al.*, Effects of UV-radiation on the cleanability of titanium dioxide-coated glazed ceramic tiles. *J. Eur. Ceram. Soc.*, 2007, **27**, 4569–4574.
6. Redsven, I., Kuisma, R., Laitala, L., Pesonen-Leinonen, E., Mahlberg, R., Kymäläinen, H.-R. *et al.*, Application of a proposed standard for testing soiling and cleanability of resilient floor coverings. *Tenside Surfact. Det.*, 2003, **40**(6), 346–352.
7. Hupa, L., Bergman, R., Fröberg, L., Vane-Tempest, S., Hupa, M., Kronberg, T. *et al.*, Chemical resistance and cleanability of glazed surfaces. *Surf. Sci.*, 2005, **584**(1), 113–118.
8. Kuisma, R., Fröberg, L., Kymäläinen, H.-R., Pesonen-Leinonen, E., Piispanen, M., Melamies, P. *et al.*, Microstructure and cleanability of uncoated and fluoropolymer, zirconia and titania coated ceramic glazed surfaces. *J. Eur. Ceram. Soc.*, 2007, **27**(1), 101–108.
9. Dondi, M., Ercolani, G., Guarini, G., Melandri, C., Raimondo, M., Rocha e Almendra, E. *et al.*, The role of surface microstructure on the resistance to stains of porcelain stoneware tiles. *J. Eur. Ceram. Soc.*, 2005, **25**(4), 357–365.
10. Minabe, T., Tryk, D. A., Sawunyama, P., Kikuchi, Y., Hashimoto, K. and Fujishima, A., TiO_2-mediated photo degradation of liquid and solid organic compounds. *J. Photochem. Photobiol. A*, 2000, **137**, 53–62.
11. Fretwall, R. and Douglas, P., An active, robust and transparent nanocrystalline anatase TiO_2 thin film – preparation, characterisation and the kinetics of photodegradation pf model pollutants. *J. Photochem. Photobiol. A*, 2001, 229–240.
12. Tenorio Cavalcante, P. M., Dondi, M., Ercolani, G., Guarini, G., Melandri, C., Raimondo, M. *et al.*, The influence of microstructure on the performance of white porcelain stoneware. *Ceram. Int.*, 2004, **30**, 953–963.
13. Guan, K., Relationship between photocatalytic activity, hydrophilicity and self-cleaning effect of TiO_2/SiO_2 films. *Surf. Coat. Technol.*, 2005, **191**, 155–160.
14. Mellot, N. P., Durucan, C., Pantano, C. G. and Gugliemi, M., Commercial and laboratory prepared titanium dioxide thin films for self-cleaning glasses: photocatalytic performance and chemical durability. *Thin Solid Films*, 2006, **502**, 112–120.
15. Kronberg, T., Ritschkoff, A.-C., Mahlberg, R., Mannila, J., Kallio, M., Vesa, A. *et al.*, Soil-resistant surfaces for traditional ceramics. *J. Eur. Ceram. Soc.*, 2007, **27**, 1775–1780.
16. Piispanen, M., Fröberg, L., Kronberg, T., Areva, S. and Hupa, L., Corrosion of glazes coated with functional films in detergent solutions. *Adv. Sci. Technol.*, 2006, **45**, 156–161.
17. Fröberg, L., Kronberg, T., Törnblom, S. and Hupa, L., Chemical durability of glazed surfaces. *J. Eur. Ceram. Soc.*, 2007, **27**, 1811–1816.
18. Piispanen, M., Määttä, J., Kronberg, T., Areva, S., Sjöberg, A.-M. and Hupa, L., Effect of mechanical and chemical wear on cleanability of functional and traditional glazed surfaces. In *Proceedings in 10th International Conference and Exhibition of the European Ceramic Society*, 2007.
19. Fröberg, L., Kronberg, T., Hupa, L. and Hupa, M., Influence of firing parameters on phase composition raw glazes. *J. Eur. Ceram. Soc.*, 2007, **27**(2–3), 1671–1675.
20. Raulio, M., Pore, V., Areva, S., Ritala, M., Leskelä, M., Lindén, M., Rosenholm, J. B., Lounatmaa, K. and Salkinoja-Salonen, M., Destruction of *Deinococcus geothermalis* biofilm by photocatalytic ALD and sol–gel TiO_2 surfaces. *J. Ind. Microbio. Biotechnol.*, 2006, **33**, 261–268.
21. Pesonen-Leinonen, E., Determination of cleanability of plastic surfaces. Academic Dissertation, University of Helsinki, 2005. ISBN: 952-10-2731-2, ISSN: 1455-4453.
22. Takeda, S. and Fukawa, M., Role of surface OH groups in surface chemical properties of metal oxide films. *Mater. Sci. Eng. B*, 2005, **119**, 265–267.
23. Takeda, S., Yamamoto, K., Hayasaka, Y. and Matsumoto, K., Surface OH group governing wettability of commercial glasses. *J. Non-Cryst. Solids*, 1999, **249**, 41–46.
24. Stevens, N., Priest, C. I., Sedev, R. and Ralston, J., Wettability of photoresponsive titanium dioxide surfaces. *Langmuir*, 2003, **19**, 3272–3275.
25. Fröberg, L., Hupa, L. and Hupa, M., Corrosion of crystalline phases of matt glazes aqueous solutions. *J. Eur. Ceram. Soc.*, 2009, **29**, 7–14.