Wettability of anatase ceramic glazes

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ABSTRACT
Coatings with catalytic properties, i.e., activated by UV radiation, can form surfaces with a number of special features, based on the ability of such coatings to interact with UV radiation. Also, they change the surface wettability and, therefore, the water that is deposited naturally or artificially on these surfaces can easily runoff. Some coatings can exhibit the hydrophilic effect, where droplets of water deposited on them decrease their contact angle with the photocatalytic surface after exposure to UV radiation, forming a highly uniform thin film of water, which behaves optically like a clear sheet of glass, avoiding the fogging of the surfaces and, therefore, making self-cleaning surfaces. The aim of this work was the study of the wettability of anatase ceramic glazes for self-cleaning tiles developed by the addition of TiO\textsubscript{2} in commercial frits. Glazes were developed by adding anatase in commercial ceramic frits as an agent of photocatalysis. The glazes were coated on ceramic tiles, which were fired between 800 and 1000°C. The formulations were characterized (SEM), and the wettability was determined by measuring the water contact angle. The microstructural analysis (SEM) showed that the anatase particles can disperse properly in the glaze matrix. The determination of the contact angle shows the clear influence of the glaze type and sintering temperature on the wettability characteristics of the obtained layer.

INTRODUCTION
The photocatalytic semiconductors have attracted much attention because they are a low cost and non-toxic alternative to develop photocatalytic surfaces that could destroy organic compounds by oxidation reactions. In addition, the semiconductor particles can be immobilized in a thin layer on any surface, and can maintain their activity after repeated catalytic cycles (1). Among the various semiconductor available, such as metal oxides (e.g. TiO\textsubscript{2}, ZnO and CeO\textsubscript{2}) and metal sulfides (e.g. ZnS or CdS), the titania (TiO\textsubscript{2}) has been the most suitable for photocatalysis and photovoltaic activity because of its relatively high quantum yield (2). Titanium dioxide has two main catalytically active crystalline phases, anatase and rutile. The anatase form is generally more photoactive and is widespread in the natural environment. For these reasons, it is widely used in commercial applications as a self-cleaning coating on exterior surfaces, as it reduces and decomposes organic pollutants, removing dirt as grease and oil, thus allowing smaller maintenance costs or efforts (3, 4). Currently there is a special interest in nanostructured materials due to their novel properties and functions related to their different electrical, mechanical, magnetic, optical, electronic and catalytic behaviour. Nanostructured titanium dioxide coatings are being developed with the aim of increasing the hardness, stiffness and mechanical strength as well as to provide resistance to corrosion and oxidation at high temperatures, with interesting antibacterial properties, besides their photocatalytic and photovoltaic properties (9-12).

Titanium dioxide is also known for properties such as chemical durability, thermal stability, high hardness, applications for white pigments and resistance to wear, being a material used for the development of protective coatings for ceramic tiles (5, 6). In fact, titanium dioxide is used as a self-cleaning coating on exterior surfaces, as it reduces and decomposes organic pollutants, removing dirt as grease and oil, thus allowing smaller maintenance costs or efforts (7, 8). Currently there is a special interest in nanostructured materials due to their novel properties and functions related to their different electrical, mechanical, magnetic, optical, electronic and catalytic behaviour. Nanostructured titanium dioxide coatings are being developed with the aim of increasing the hardness, stiffness and mechanical strength as well as to provide resistance to corrosion and oxidation at high temperatures, with interesting antibacterial properties, besides their photocatalytic and photovoltaic properties (9-12).

Therefore, the aim of this research was the development of glazes for protection and coverage of ceramic tiles for facades of buildings. The ceramic tiles – tiles for building facades – firstly undergo a conventional manufacturing process and in sequence a special layer of glaze can be applied on their surfaces, giving them various properties that make them functional coatings. The process of using an already fired ceramic tile and the application and burning of a new layer (glaze) is currently used in the ceramic industry, a process called “third firing”, usually used with aesthetic functions, such as application of metallic surfaces. Coatings with catalytic properties, i.e., that can be activated by UV radiation, can form surfaces with a number of special features, based on the ability of such coatings to interact with UV radiation, and also change the surface wettability and facilitate water runoff that is deposited naturally or artificially on these surfaces (13-15). Due to their inorganic nature coatings with catalytic properties are non-combustible and are resistant to conventional cleaning agents. As indicated, the properties of these coatings are activated by UV radiation, which produces a series of internal changes in the electronic structure of the coating, but does not affect its appearance and the technical characteristics of its macroscopic surface (hardness, chemical resistance, etc.). The UV radiation is present in daylight (even without direct sunlight) and partly in some artificial light sources. Therefore, this type of coating is particularly suitable for exterior and interior areas exposed to enough natural light, or with adequate artificial light sources. The activating effect generated on the surface does not disappear immediately when the radiation ceases, but lasts for a sufficiently long time (longer than the night period) to ensure their effectiveness (16-18). In addition, some of these coatings significantly increase the contact angle between the work piece surface and water, thereby favouring the formation of drops in which dust particles adhere. The drops easily slide on this surface, bringing the dirt and helping to keep the surface free of inert material (dust, dried vegetable debris, etc.). This effect provides other type of functionally
to photocatalytic coatings, to keep surfaces clean, avoiding also the proliferation of microorganisms. The hydrophobic coatings used on glass surfaces consist of a combination of organic and inorganic materials with nanometric dimensions, which increase the surface tension, thus contributing to the properties of the surface on which they were applied. Other coatings exhibit the hydrophilic effect, where droplets of water deposit on them decrease their contact angle with the photocatalytic surface after exposure to UV radiation, forming a highly uniform thin film of water, which behaves optically like a clear sheet of glass, avoiding the fogging of the surfaces (19-28). Therefore, the objective of this work was the development of photoactive anatase glazes (TiO₂) for self-cleaning ceramic tiles. Initially, the wettability of the anatase glazes was measured after UV irradiation in order to determine the self-cleaning effect of the coatings. More experiments are being conducted to determine the photo catalytic activity of the glazes.

EXPERIMENTAL PROCEDURE

In this work two commercial ceramic frits (with low softening point), halite (NaCl) and commercial anatase were used. The frits were chemically (XRF and AAS for B element) and thermally (optical dilatometry, 40°C/min, air atmosphere) characterized. For anatase, the chemical composition (XRF), particle size (laser diffraction), and crystallite structure (XRD, Cu Kα, l = 1.5418 Å), 40 kV and 30 mA, 2θ from 10 to 90°, 0.05° step and 1 s time) were determined. The photoactive glazes formulations were prepared with a 3:7:10:80 ratio of TiO₂, frit or halite, dispersant and water (all mass percent) respectively, and the formulations were vigorously stirred for subsequent deposition on ceramic tiles. The suspensions were applied by spraying on already glazed stoneware tiles (10 cm × 10 cm), and the tiles were fired between 800°C and 1000°C in 1 h cycle in a laboratory muffle furnace. After firing, the tiles were characterized by scanning electron microscopy (SEM). The hydrophilic (or hydrophobic) effect of adding anatase to the ceramic glaze was determined by measuring the water contact angle of on the tile surface at different UV-irradiation times with a contact angle goniometer system.

RESULTS AND DISCUSSION

The particle size distribution and the X-ray diffractometry of the anatase powder are shown in Figure 1. The anatase powder shows mean diameter of 300 nm, being a submicron powder. Also, the powder is formed by a mixture of anatase (89 percent) and rutile (11 percent) phases. Therefore, suitable for photocatalytic application (3, 16-20). The chemical analysis (XRF and AAS) of the frits is shown in Table 1. TEC frit is a borosilicate glass with sodium and zinc oxides; the loss on ignition is probably due to the presence of water. The SMT frit is composed by silica and calcium oxide with a small addition of borate and sodium and potassium oxides; the presence of higher alumina content shows that this frit presents a higher softening point. Halite is a salt (NaCl, 99 percent purity). The thermal behaviour of TEC and SMT frits and halite determined by optical dilatometry is shown in Table 2. TEC frit is more adequate to a third-firing process than SMT due to its lower softening and melting temperatures as a result of its chemical composition. The SMT frit is more refractory than TEC frit because of its higher content in alumina and silica and lower content in borate, besides the high content in calcium oxide. In turn, the halite shows intermediate behaviour between the TEC and SMT frits, with a small gap between the sintering and melting points, not suitable for industrial use due to the great viscosity variation in a small temperature gradient. In addition, the release of Cl species during firing promotes the formation of HCl and subsequent corrosion of all machinery. Although widely used in the fabrication of industrial frits in Brazil, the use of halite is not appropriate in the ceramic industry. Regarding the TiO₂ powder, the XRD analysis has confirmed that it is mostly composed of anatase (90 percent by Rietveld analysis). The particle size distribution analysis shows that the anatase powder is submicron, what is not interesting for promoting photocatalytic activity, since the photocatalytic activity is a function of the crystal phase and size. A nanocrystalline anatase phase would be preferred.

Figure 2 shows SEM images of the surfaces of the ceramic tiles after application of the anatase modified glazes and third-firing. At 800°C a) the glaze composed by TEC frit and anatase is partially stretched over the tile surface, covering the whole surface of the sample, resulting in some roughness. There are small particles on the surface. At 900°C b) porosity and surface crystallization are present on the sample’s surface. Porosity is related to evaporation of some constituent of the glaze. The crystallization is due the effect of ZnO and anatase, noting that TiO₂ (anatase) has a strong effect as crystallization agent. Therefore, at 800°C there is formation of a glaze layer with proper texture. With respect to the glaze formed with halite and anatase, at both temperatures 800°C c) and at 900°C d) there was no homogeneous layer that could cover the entire surface of the tiles – the glaze apparently did not softened or stretched on the ceramic tiles surface, remaining only as a pre-glaze on the surface of the sintered samples. The glaze composed by the SMT frit and anatase even at 1000°C has not formed an even surface (not shown). The wetting test was used to determine the effect of anatase addition on ceramic frits forming anatase-modified glazes on the surface of the tiles after third-firing. Photocatalytic tests are still on-going. Figure 3 shows the variation of water contact angle depending on the type of frit used in the glaze and the firing temperature without UV irradiation. Without the modified glazes, the water contact angle with the original surface of the glazed tile is close to 10°. Without UV irradiation, the halite/anatase glaze fired up to 900°C shows a hydrophilic behaviour, with water contact angle less than 10°. At 950°C firing temperature the glaze becomes more hydrophobic, with water contact angle of 35°. Almost no substances show contact angles lower than 10° with the exception of some water-absorbing surfaces. Thin films composed of titanium oxide photocatalyst show hydrophilic behaviour only after exposition to UV light. The SMT/anatase glaze shows hydrophilic behaviour only at 800°C firing temperature and the TEC/anatase glaze do not show hydrophilic behaviour at any firing temperature. For all glazes, the increasing firing temperature promotes the increasing of water contact angle, without UV exposition.
Once more, for all glazes, the increasing firing temperature promotes the increasing of water contact angle after UV exposition. With increasing UV exposition time the SMT/anatase and halite/anatase glazes show hydrophilic behaviour [contact angle<10°] at low firing temperatures. Figure 4b shows marginal hydrophilic behaviour at low firing temperatures. There are two possibilities for the decreasing in the water contact angle after long periods of UV irradiation: first, the samples present photocatalytic behaviour, and the mixing of anatase powder with low softening temperature frits was successful; or second, at low temperatures the glaze was not completely melted on the surface and after long periods of UV exposition the surfaces were cleaned and water was absorbed by the pores of the non-melted glaze. This is a preliminary study. The photocatalytic behaviour of the studied glazes is being determined in order to correlate (or not) the hydrophilic effect with photocatalysis induced by the anatase crystals present in the ceramic glazes.

**CONCLUSION**

Ceramic glazes were prepared with a sub-micron anatase powder and low melting temperature frits. The glazes were applied on grès tiles and fired between 800 and 1000°C and the fired samples were test for hydrophilic behaviour. The main results are:

1. After firing the anatase powder seems to be very well dispersed in the glaze matrix.
2. The SMT/anatase and halite/anatase glazes show hydrophilic behaviour [contact angle<10°] at low firing temperatures after UV irradiation;
3. The apparent hydrophilic behaviour may be explained by the porosity of the glazes at low firing temperatures, as the long irradiation time probably is cleaning the tiles surface and promoting water absorption.

**ACKNOWLEDGMENTS**

The authors thank the Instituto de Tecnologia Cerâmica (ITC, Castellón) for the contact angle measurements and CAPES (Brasil) for the scholarship provided.

**REFERENCES AND NOTES**