

## DEVELOPMENT OF TiO<sub>2</sub> WHITE GLAZES FOR CERAMIC TILES

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### ABSTRACT

*The objective of this work was the use of titania polymorphs (rutile and anatase) in substitution to zirconia as the main component to cause white opacity in ceramic glazes for tile coatings. Initially the total zirconia (12% in mass fraction) was replaced in the standard frit by rutile and by anatase in mass fractions of 5%, 10% and 15%, forming two frit groups. The frits were melted at 1450°C and quenched in water. Each frit was ground in eccentric mill with the addition of 10% of kaolin, 0.2% of sodium tripolyphosphate, 0.2% of carboxymethylcellulose and 30% of water, forming a glaze slurry with 1.80g/cm<sup>3</sup> density and viscosity of 50s in Ford cup n° 4. The glazes were applied in layers of 4mm thickness over previously engobed and fired tiles in two thermal cycles: 1117°C during 22min and 1130°C during 27min, both in roller kiln. The colour of all the glazes was analyzed by spectrophotometry (400nm to 700nm) and the formed phases by x-ray diffraction (XRD CuKα) and scanning electronic microscopy (SEM). The results showed the frit with 10% anatase formed a totally white glaze with great coating capacity. The frits with rutile caused yellow opacity. The results of microscopy and x-rays diffraction revealed that the opacity is caused by tiny rutile crystals in the anatase frits and by titanate crystals in the rutile frits.*

## 1. INTRODUCTION

The white and opaque glaze coatings are used in the tile ceramic industry to form a base on which layers of serigraphy can be applied. Traditionally, the industrial glazes for ceramic tiles have used zircon or zirconia as opacity agents for coating, the former being much more used due its smaller cost. However, even using a large amount of zirconia not always the best results are obtained, showing that zirconia only yields a white coating when used in greater amounts. The use of titanium oxide as a white coating is not new, and it has been used for decades to glaze porcelains and metals. But there is a belief in the tile industry that  $\text{TiO}_2$  only causes a yellowish opacity, and it is not adequate for use in white coating glazes.

In the nineteenth century titanium compounds were known fluxes for porcelain glazes and crystallites of  $\text{TiO}_2$  formed during firing generated opacity, however, not yielding white coatings<sup>[1]</sup>. Impurities (Fe, Cr, etc.) present in the raw materials produced non-white coats until purer forms of  $\text{TiO}_2$  became available<sup>[2]</sup>. Some studies reported the relationship between  $\text{TiO}_2$  crystallite size and shape and the resulting reflectance and colour, identifying rutile and anatase phases, with the acicular rutile particles occurring at higher temperatures or longer firing times and the rounded anatase particles forming earlier in the firing process<sup>[3]</sup>. The blue colour was associated with the smaller and rounded anatase particles and the yellow colour formed at the later stages of firing was associated with the dissolution of the anatase particles at the expense of the larger rutile particles. The colour change (blue to yellow) corresponds to a large increase in the rutile/anatase ratio<sup>[3]</sup>.

TEM studies confirmed that rutile crystals were always present with an acicular morphology; however, anatase crystals were observed with cubic, rectangular and acicular morphologies<sup>[4]</sup>. Also, anatase nucleation is a bulk phenomena and rutile nucleation occur at the interface between adjacent frit particles<sup>[5]</sup>. The depletion of anatase crystallites near rutile surface crystals indicates that the anatase to rutile inversion is a ripening process as opposed to a phase transformation. Nucleation (at  $425^\circ\text{C}$ ~ $460^\circ\text{C}$ ) and growth rates (at  $620^\circ\text{C}$ ~ $720^\circ\text{C}$ ) control the resultant crystal phases and morphologies<sup>[6]</sup>. Also, temperature exhibits a greater effect than time on glass viscosity and growth rates for  $\text{TiO}_2$ -opacified enamels<sup>[2]</sup>. The thermal history of the porcelain enamel has a two or three times greater effect on the measured viscosity. Thus, the consistency of the smelting and quenching process for the manufacture of  $\text{TiO}_2$ -opacified frits is even more important than for many other porcelain enamels and glazes.

Some studies tried to predict the rutile to anatase concentrations in  $\text{TiO}_2$ -opacified coats as function of time and temperature<sup>[7]</sup>. The crystallization of anatase, crystallization of rutile and conversion of anatase to rutile, besides solubility factors (similar to the precipitation of salts from solutions) could be used to predict the crystal concentrations under most conditions, except short time and low temperature conditions, but the observed colour data did not correlate well with the observed, or predicted, crystalline concentration data<sup>[8,9]</sup>. Regarding the porcelain glaze physical properties (as viscosity) to resultant reflectance and colour, porcelain glazes produce reflectance via opacifiers, including crystallites (such as  $\text{TiO}_2$  or  $\text{ZrO}_2$ ) but may also include insoluble materials, phase separated glasses and gas bubbles. The items which control the opacity in porcelain glazes are<sup>[10]</sup>: index of refraction difference between the glass and opacifier; absorption of the glass and opacifier; sizes and shapes of the opacifier; distribution of the opacifier; number of particles; wavelength of the incident light; and porcelain glaze (or enamel) thickness<sup>[10]</sup>.

High indices of refraction for  $\text{TiO}_2$  (rutile: 2.76 and anatase: 2.52) compared to that of typical porcelain glazes (1.50 to 1.55) make  $\text{TiO}_2$  the best selection for opacification of glazed ceramics<sup>[10]</sup>. Other typical opacifiers,  $\text{SnO}_2$  (2.04),  $\text{Sb}_2\text{O}_3$  (2.09) and  $\text{ZrO}_2$  (2.17) are not

as effective as  $\text{TiO}_2$ . There are numerous compositional effects on  $\text{TiO}_2$ -opacified porcelain glazes<sup>[10,11]</sup>.  $\text{Na}_2\text{O}$  is preferable to  $\text{K}_2\text{O}$  for flow, colour and reflectance, with  $\text{K}_2\text{O}$  causing a decrease in viscosity, resulting in more anatase crystals and a bluish-white colour.  $\text{K}^+$  has been used to stabilize the anatase phase in pigment research<sup>[12]</sup>.  $\text{P}_2\text{O}_5$  enhances the blueness of porcelain glazes through an acceleration of anatase formation relative to rutile. Both crystals exhibit enhanced nucleation rates, but anatase is accelerated by twice that of rutile. So  $\text{PO}_4^{3-}$  is used to stabilize the anatase structure<sup>[12-14]</sup>. Sb and Nb additions enhance the blueness of titania-opacified glazes, probably because these elements retard crystal growth, producing a coating with smaller crystals and a large number of anatase crystals<sup>[15]</sup>. A reduction in viscosity and an improvement in acid resistance are other beneficial effects of  $\text{TiO}_2$  additions to porcelain glazes and enamels<sup>[16]</sup>:  $\text{TiO}_2$  was shown to decrease the viscosity of all porcelain glazes except high (>20%)  $\text{P}_2\text{O}_5$  compositions. Only additions of <11%  $\text{TiO}_2$  reduces the viscosity and greater amounts increases it<sup>[17,18]</sup>.

In addition to time/temperature relationships and compositional effects, numerous other factors can affect the crystallization and resultant reflectance and colour of porcelain glaze coatings. The two other major influences are mill additions and furnace atmosphere conditions. Mill additions can directly influence the viscosity of the porcelain glaze as well as the oxidation/reduction conditions in the coating. Both effects will change the fired coating<sup>[19,20]</sup>. The furnace atmosphere can also change the oxidation/reduction conditions, and can alter the glass viscosity through moisture variations. These process variables all lead to tight controls on production conditions and specialized development of coating systems for most glazing plants on an individual basis.

## 2. EXPERIMENTAL PROCEDURE

Initially the total zirconia (12% in mass fraction) was replaced in the standard frit by rutile and by anatase in mass fractions of 5%, 10% and 15%, forming two frit groups (table 1). The frits were melted at 1450°C and quenched in water. Each frit was ground in eccentric mill with the addition of 10% of kaolin, 0.2% of sodium tripolyphosphate, 0.2% of carboxymethylcellulose and 30% of water, forming glaze slurries with controlled density (1.80g/cm<sup>3</sup>) and viscosity of (50s flowing time in Ford cup n° 4). The glazes were applied in layers of 0.4mm thickness over previously engobed tiles and fired in two thermal cycles: 1117°C during 22min and 1130°C during 27min, both in roller kiln ("monoporosa" fast firing heat treatment). The colour of all the glazes was analyzed by spectrophotometry (400nm to 700nm) and the formed phases by x-ray diffraction (XRD  $\text{CuK}\alpha$ , 0° to 75°, 0.02°/min) and scanning electronic microscopy (SEM).

FORMULA	STANDARD	5%	10%	15%
$\text{SiO}_2$	62.3	63.1	60.7	56.3
$\text{Al}_2\text{O}_3$	4.7	5.0	4.7	4.3
CaO	7.4	7.9	8.2	7.2
$\text{Na}_2\text{O}$	13.2	4.8	5.1	4.9
$\text{K}_2\text{O}$	0.6	0.1	0.5	0.4
$\text{ZrO}_2$	12.0	-	-	-
$\text{TiO}_2$	-	5.0	10.0	15.0
MgO	1.4	0.0	1.4	0.0
$\text{Fe}_2\text{O}_3$	0.8	0.1	0.1	0.1
$\text{B}_2\text{O}_3$	4.8	5.2	4.9	4.7

Table 1. Compositional formulas for the studied frits ( $\text{TiO}_2$  for rutile and anatase frits)

### 3. RESULTS AND DISCUSSION

Figure 1 shows the glazes with 10% wt. TiO<sub>2</sub> (anatase and rutile) fired at 1117°C/22min and at 1130°C/27min. The standard zirconia glaze (12% wt. ZrO<sub>2</sub>) is the central sample. At 1117°C/22min cycle both glazes (anatase and rutile) present a yellowish coating, but at 1130°C/27min cycle the yellow appearance diminishes for both glazes, showing the influence of temperature and time in the crystal formation – and in glaze opacity. At 10% anatase and rutile addition the yellow tonality diminishes for both glazes at 1117°C/22min. Both glazes have a major covering effect comparing the standard zirconia glaze. But at 1130°C/27min cycle the anatase glaze is visually whiter than the standard zirconia glaze. Finally, at 15% titania addition a complete coating is obtained for both glazes at both firing cycles (1117°C/22min and 1130°C/27min) comparing to the zirconia standard. But at this point both glazes are again yellowish.

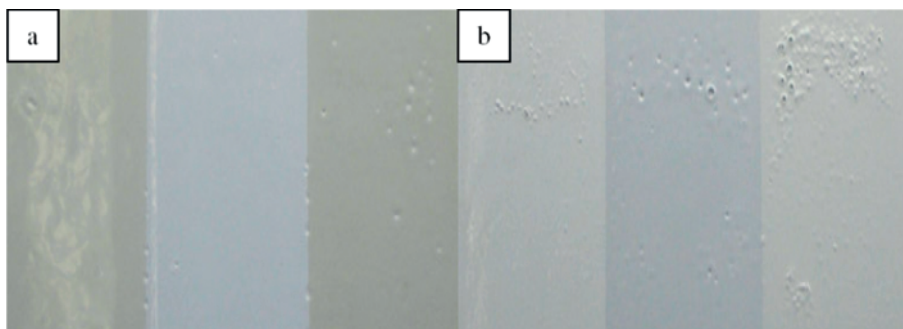


Figure 1. Glazes with 10% anatase (left) and rutile (right) addition fired at (a) 1117°C/22min and at (b) 1130°C/27min. The central sample is the standard zirconia glaze

At 1117°C/22min cycle all glazes are more opaque than the standard, except for 5% anatase and rutile addition, figure 2. The reflectance for 10% and 15% anatase and rutile glazes is greater than the standard reflectance, beginning at 420nm, showing the more effective covering effect of these glazes. But the reflectance of these glazes diminishes at violet and blue wavelengths (400nm to 500nm) and increase at higher yellow and red wavelengths (600nm to 700nm), what justifies the yellowish tonality of these glazes.

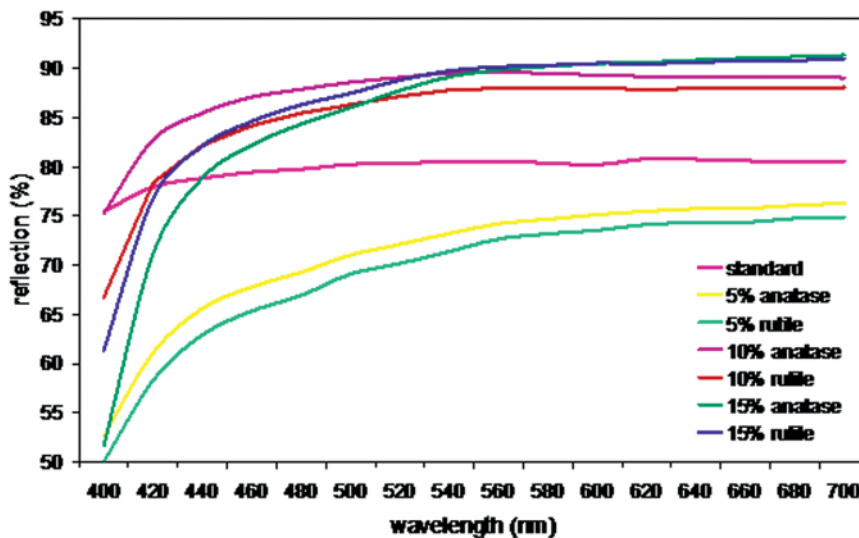


Figure 2. Reflectance spectra for 5%, 10% and 15% anatase and rutile glazes fired at 1117°C/22min cycle

At 1130°C/27min once more the 5% anatase and rutile glazes have minor covering effect than the zirconia standard glaze, figure 3. The 10% and 15% glazes (anatase and rutile) are more opaque than the standard, with a higher reflectance in comparison with the zirconia glaze. The anatase glaze presents a straighter curve for all wavelengths, mainly for the violet and blue regions (400nm to 500nm), explaining its whiter behaviour regarding the standard glaze, figure 3.

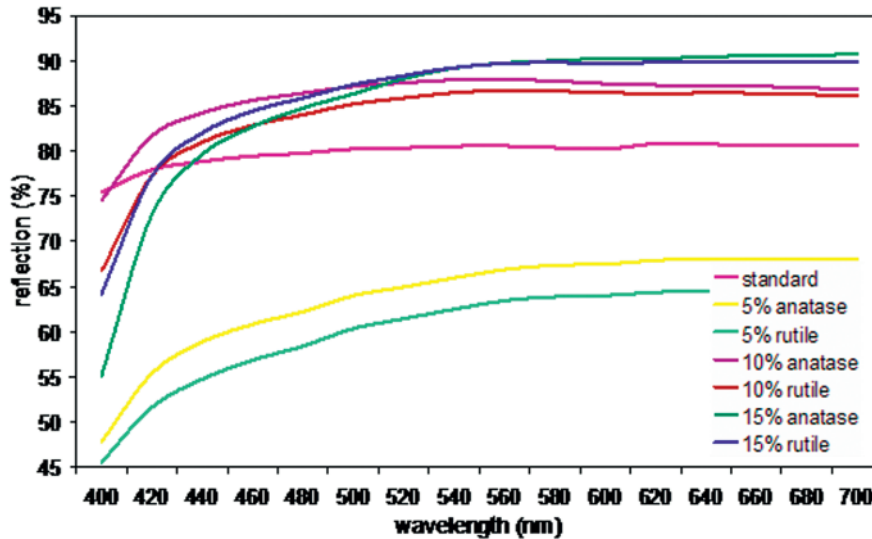


Figure 3. Reflectance spectra for 5%, 10% and 15% anatase and rutile glazes fired at 1130°C/27min cycle

As the opacity of white glazes is obtained by crystallization of the glass system, the yellow or white opacity of titania glazes is explained by the phases developed during glaze heat treatment. Figure 4 shows the XRD results of the standard glaze in comparison with the 5% anatase and rutile glazes for both firing cycles (1117°C/22min and 1130°C/27min). At 1117°C/22min the standard glaze is the only one with well developed crystalline phases; the glazes with 5% anatase and rutile additions did not present well defined crystalline phases, what justifies their poor covering properties showed by their reflectance curves. Just quartz crystallizes in the 5% anatase glaze at 117°C/22min cycle, but titanite (titanium and calcium silicate) develops in the rutile glaze. At 1130°C/27min  $\alpha$  quartz is more crystallized in the anatase glaze and titanite in the rutile glaze.

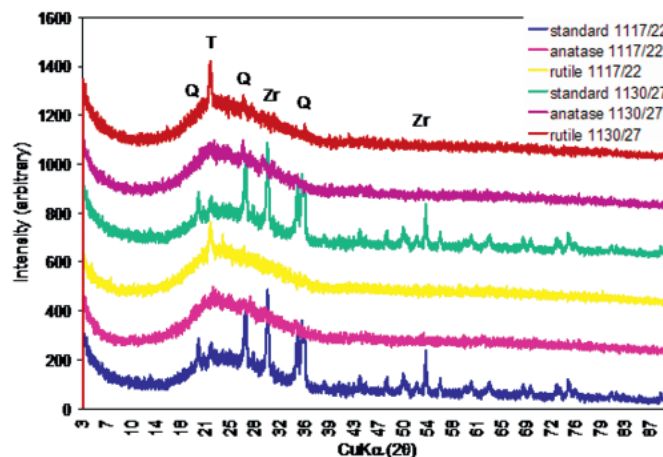


Figure 4. XRD patterns for 5%  $\text{TiO}_2$  addition (anatase and rutile glazes) at 1117°C/22min and 1130°C/27min firing cycles (Q=quartz; T=titanite; Zr=zircon)



The XRD results for the 10% anatase and rutile glazes is shown in figure 5. At 1117°C/22min the rutile glaze develops titanite phase and a reduction in the  $\alpha$  quartz phase; the anatase glaze develops titanite and anatase, with a reduced  $\alpha$  quartz. At 1130°C/27min the anatase phase remains in the anatase glaze and titanite in the rutile glaze, what can explain the yellow colour of the rutile glaze.

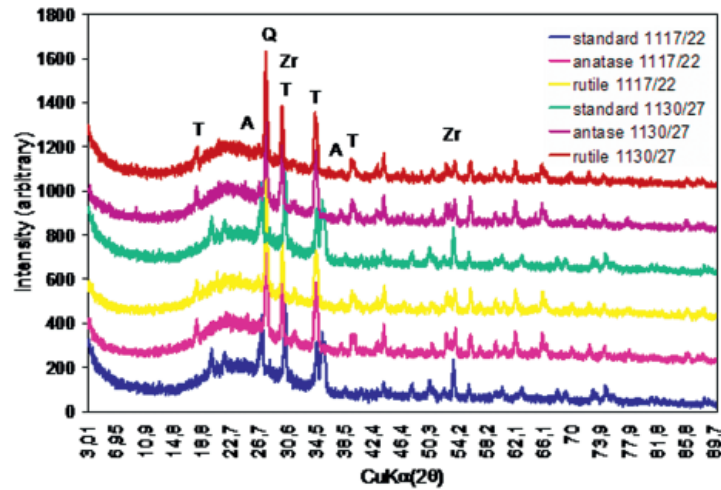


Figure 5. XRD patterns for 10% TiO<sub>2</sub> addition (anatase and rutile glazes) at 1117°C/22min and 1130°C/27min firing cycles (A=anatase; Q=quartz; T=titanite; Zr=zircon)

The XRD results for the 15% anatase and rutile glazes is shown in figure 6. At 1117°C/22min the rutile glaze develops mainly titanite and the anatase glaze develops titanite and rutile, with relicts of anatase and  $\alpha$  quartz. Both glazes present well developed crystalline phases even when compared to the standard zircon glaze. At 1130°C/27min the anatase phase completely disappears from both glazes, being a transitory phase. The rutile glaze presents titanite; the anatase glaze presents titanite and rutile, and again the yellowish appearance.

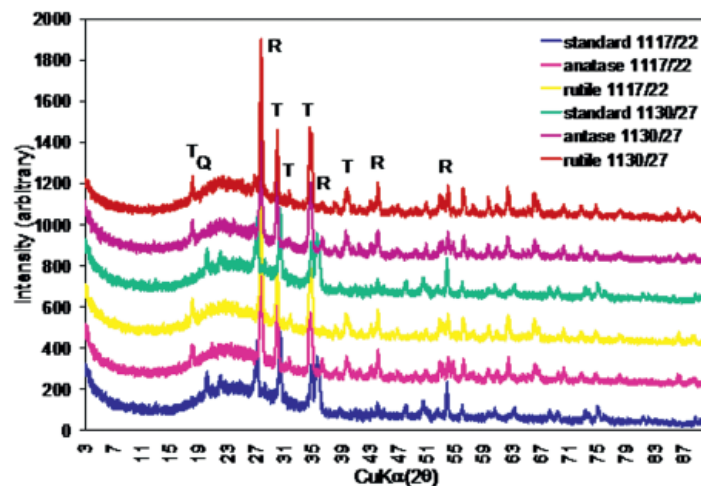


Figure 6. XRD patterns for 15% TiO<sub>2</sub> addition (anatase and rutile glazes) at 1117°C/22min and 1130°C/27min firing cycles (A=anatase; Q=quartz; T=titanite; Zr=zircon)

Finally, figure 7 shows the microstructure of the 15% rutile glaze fired at 1117°C/20min. The round particle is titanite and the needle-like particles are rutile.

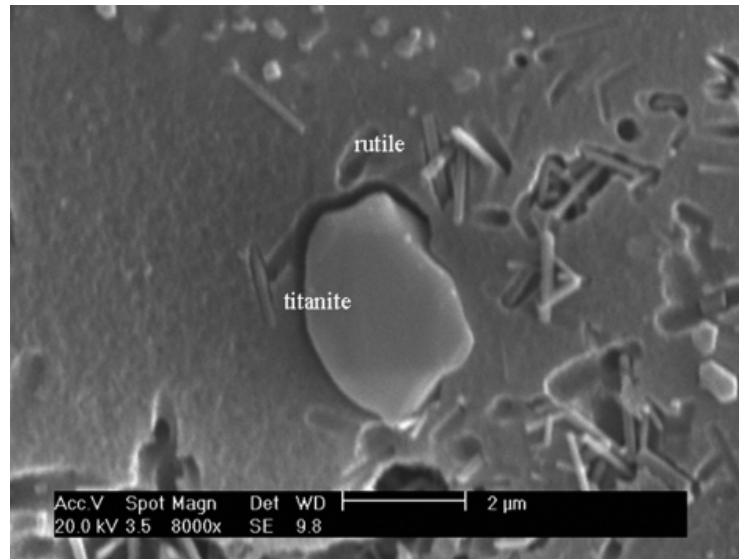


Figure 7. SEM microstructure of the rutile glaze fired at 1117°C/20min

#### 4. CONCLUSION

The presence of  $\text{TiO}_2$  in ceramic glazes starts their crystallization because  $\text{TiO}_2$  is the first oxide system to precipitate in the liquid glass, acting as a nucleating agent and forming rutile and anatase (when in a pure form) and other phases as quartz and titanite. Apparently anatase is the most efficient as nucleating agent: in the beginning the anatase frit forms anatase at low temperatures; at higher temperatures the anatase phase transforms to rutile, and rutile forms titanite. The rutile frit forms titanite directly, the crystalline phase that results in the yellow appearance of titania glazes. So the use of titanium oxide in the anatase form is very efficient to obtain white glazes, and a 10% addition results in great opacity, better than the zircon glaze used in this study.

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