EFFECT OF THE ANATASE ADDITION ON THE CHARACTERISTICS OF A GLAZE CONTAINING DOLOMITE

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INTRODUCTION

Anatase is a raw material that is widely used as an opacifier in preparing white opaque glazes for ceramic floor tiles. Anatase is known to produce variations in glaze colour, opacity and gloss, depending on the proportion used, while these variations are also related to the type and amount of the other glaze composition constituents[1]. It was therefore considered of interest to attempt to ascertain why these phenomena arise, to be able to regulate the factors mentioned on a well-reasoned basis, and obtain products exhibiting constant, controlled characteristics.

EXPERIMENTAL

A series of compositions was prepared by adding different anatase proportions to a base formula composed of a single-fire frit that yielded transparent glazes, and dolomite. The effect was thus concurrently determined of dolomite on the properties of the glazes prepared with anatase. Table I details all the tested compositions.

Components	STD	1	2	3	4	5
Frit	90	87	84	81	91	85
Dolomite	10	10	10	10	--	--
Anatase	--	3	6	9	9	15

Table 1. *Tested compositions.*

[1]. SHAW, K. *Ceramic glazes*. Amsterdam: Elsevier, 1971.

These six compositions were used to prepare a further six suspensions under standard conditions, which were subsequently applied to a biscuited body, and fired at a peak temperature of 1100 °C with a 6 min dwell. The chromatic coordinates (L*, a* and b*), whiteness index, yellowness index and specular gloss were determined of the resulting glazes. Finally, fusion buttons were formed of compositions STD, 3, 4 and 5, and fired at a peak temperature of 1100°C, according to the same firing schedule used for the glazed specimens. The crystalline species present were then determined by X-ray diffraction. Table 2 details the chromatic coordinates, whiteness index, yellowness index and gloss of the resulting glazes.

The STD composition was glossy and quite transparent as was to be expected in view of its composition. However, it exhibited a slight opacity attributable in principle to the action of the dolomite added to the frit. The results obtained on running XRD analysis of glaze STD help explain this fact, as the technique detected the crystalline species diopside in the glaze. Diopside ($2SiO_2 \cdot CaO \cdot MgO$), whose low refractive index (1.68)[2] explains the glaze's slight opacity, arose by devitrification in firing from the glassy phase enriched with calcium and magnesium as a result of the dissolution of the CaO and MgO contained in the starting dolomite.

Composition	L*	a*	b*	I_b	I_a	R(‰)
STD	59.0	5.3	5.9	37.6	22.9	99.5
1	57.5	6.6	-7.7	71.0	-16.0	104.8
2	83.8	0.3	-1.6	84.5	-3.1	97.9
3	90.0	-0.5	0.9	84.8	1.5	71.3
4	89.0	-0.6	0.1	85.8	0.0	84.0
5	92.0	-1.1	4.2	77.4	7.6	5.4

Table 2. Whiteness and specular gloss.

The introduction of anatase produced a series of modifications in the glaze characteristics as the anatase proportion was raised. In the first place, on adding small amounts (composition 1), a marked increase was observed in the bluish hue of the glaze (b*), with hardly any change in opacity or gloss. This was likely to be due to immiscible-liquid phase separation arising in glazes containing titanium, when it passed into the glassy phase as a result of anatase dissolution in firing. In this case, titanium crystalline phase devitrification did not occur owing to the minor proportion of titanium in this composition[3], [4].

On raising the anatase addition, while keeping the dolomite proportion constant (compositions 2 and 3), opacity was observed to increase noticeably (L*), with a drop in the bluish hue (b*) and gloss (R). XRD analysis of sample 3 revealed the presence of diopside (in the same proportion as in the STD sample) and sphene ($SiO_2 \cdot TiO_2 \cdot CaO$). This suggests that the rise in titanium occurring in the glaze when anatase dissolved was large enough to allow it to combine with the calcium and silicon present, and form a crystalline phase (sphene), which arose in the glaze by devitrification. As the refractive index of sphene is relatively high (1.90)[2], the degree of opacity grew appreciably compared to that of the compositions in which this crystalline species did not appear. The opacity (whiteness) moreover progressively hid the bluish hue caused by phase separation.

[2]. KLEIN, C.; HURLBUT, C.S. *Manual de mineralogía.* 4ª ed. Barcelona: Reverté, 1996.
[3]. MCMILLAN, P.W. *Glass-ceramics.* 2nd ed. London: Academic Press, 1979.
[4]. SCHOLZE, H. *Glass: nature, structure, and properties.* New York: Springer-Verlag, 1991.

Finally, with regard to compositions 4 and 5, the following deserves highlighting. The opacity of both was similar, however the yellow hue increased (I_a) and there was a very important drop in gloss on going from 4 to 5. XRD analysis of these samples revealed the presence of sphene in sample 4 (major phase), and small amounts of rutile; sphene was also found in 5 (in a greater proportion than in 4) with a larger amount of rutile. It would therefore appear that on raising the amount of titanium contributed to the glassy phase when anatase dissolves, comes a moment when there is excess titanium in respect of the calcium present, which then produces additional rutile devitrification, the stable crystalline phase of TiO_2. This phenomenon starts appearing in composition 4 (9% TiO_2) and is especially noticeable in 5 (15% TiO_2). As rutile has a yellowish hue[1], raising its proportion in the glaze raises the yellow hue, although opacity scarcely varies as rutile has a high refractive index (2.76)[2]. Furthermore, rutile crystal size is larger than that of sphene, giving rise to a greater roughness of the glaze and hence lower gloss. No diopside was detected in these two samples as dolomite had not been used in either as a starting raw material.

[1]. SHAW, K. *Ceramic glazes*. Amsterdam: Elsevier, 1971.
[2]. KLEIN, C.; HURLBUT, C.S. *Manual de mineralogía*. 4ª ed. Barcelona: Reverté, 1996.