OBTAINING SMOOTH, WHITE FLOOR TILE GLAZES FROM ZIRCONIUM-FREE FRITS

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ABSTRACT

White glaze coatings found in current floor tile manufacture are usually produced from a mixture of frits (in a proportion of generally less than 50%), and natural crystalline aggregates (zircon, kaolin, feldspars, corundum, etc.).

This study presents the characteristics of white glazes obtained from a mixture that only consists of frits (without zircon) and kaolin. The Hunter whiteness index, gloss and other technical characteristics of the resulting glaze coatings were comparable to those exhibited by the white floor tile glazes that are currently produced using blends containing proportions of around 10% zircon and 30-50% frit.

1. INTRODUCTION

1.1. SINGLE-FIRE FLOOR TILE GLAZE CHARACTERISTICS

Single-fire floor tile glazes are generally obtained by applying different layers of material by the wet method (dripping, spraying, screen printing) or by the dry method (granulars, agglomerates) onto an opaque, white, base. Others practically consist of a base glaze of varying colours and textures (matt, satin, granular, rustic, semi-glossy), depending on the formulation. In both cases, the glaze surface never exhibits specular gloss, since any other texture is more suitable for achieving requisite glaze characteristics (abrasion, scratch, slip resistance, etc.).

Base glaze formulations usually contain frits of different nature in varying proportions (30-60%), and other non-fritted constituents (usually crystalline aggregates) of very different natures and characteristics, in accordance with the targeted final glaze properties. Some of these constituents such as feldspars, nephelines, and zinc oxide contribute together with the frits to forming the glassy matrix of the glaze. Others, however, like zirconium silicate and corundum hardly dissolve in the glassy phase. Their function is to enhance glaze abrasion resistance to a certain extent, besides acting as opacifying ($ZrSiO_4$) or matting agents (Al_2O_3).

Other frequent additions to these glazes are certain alkaline earth oxide bearing minerals (wollastonite and calcium and/or magnesium carbonates) that act as matting agents and contribute to forming glassy phase.

The main trends in the evolution of these glazes have been as follows:

- Reduction in the number of frits used for producing the base glaze, simplifying glaze preparation.
- Introducing newly developed frits into base glaze formulations, progressively increasing frit content to enhance glaze properties.
- Striving to improve product properties, making products better suited to service applications.

With regard to this last point, although at present glazes are available with high mechanical performance (high hardness and abrasion resistance), there is a clear tendency towards developing new, smoother glazes, which behave appropriately in heavily trafficked areas.

This requires producing glazes without any apparent porosity, with low sealed porosity, containing a high proportion of microcrystals of high hardness, strongly bonded (without stresses of a mechanical or thermal origin) to a glassy matrix that is also hard and resistant.

1.2. RESEARCH OBJECTIVE

The present study was undertaken to obtain glossy or matt, smooth white zirconium-free glazes for ceramic floor tiles, with technical properties resembling or closely approaching those of currently available commercial glazes, by using a blend consisting of one or more frits and a kaolin proportion of 6-8% (without further crystalline aggregates) as raw materials.

1.3. SELECTION CRITERIA OF THE FRIT COMPOSITION TO BE USED FOR PRODUCING OPAQUE WHITE GLAZES

For a glaze to be opaque it needs to be made up of two or more glassy or crystalline phases that exhibit different refractive indices. Opacity is due to the interaction of light with a heterogeneous medium. Thus, the greater the difference between the refractive indices of the constituent phases, the higher the opacity. In glazes with immiscible-phase separation, the phase compositions do not usually differ very much, so that their refractive indices are usually not very different either. Greater opacity could therefore be obtained in a glaze containing disperse crystalline phases in a glassy matrix: a continuous and a disperse phase, as long as the crystalline phase had a sufficiently different refractive index from that of the glassy phase that contained it. The number and size of the inclusions dispersed in the glassy matrix also affect opacity. The larger the proportion of disperse phase and the smaller the inclusions, the greater will opacity be, provided that the size is not smaller than the visible light wavelength, as the glaze will in this case be transparent[1].

A frit was therefore required in which firing of the consolidated layer of frit particles would produce devitrification of one or more crystalline phases, yielding a heterogeneous glaze made up of disperse crystals in a glassy matrix

The refractive index of a glass depends on its composition; equations are to be found in the literature that allow estimating this[1]. However, in the case of ceramic glazes, the refractive index of the residual glassy phase has been shown to vary very little with composition, fluctuating between 1.5 and 1.6. Consequently, the greater the difference between the crystalline phase refractive indices and these values, the higher will resulting glaze opacity be.

On the other hand, if white glazes are to be produced, the starting frit composition should contain no chromophore ions.

A literature survey was performed[2, 3] to find crystalline phases with a high refractive index, containing no colouring ions, composed of oxides that are typically part of ceramic frit compositions. This yielded the following information:

The highest refractive indices corresponded to rutile (2.61) and anatase (2.60). However rutile, which is the stable phase at high temperatures (in firing anatase turns into rutile) and remains as such at low temperature (in cooling it does revert back into anatase), provides yellow hues, so that its presence is not recommendable if white glazes are sought.

The zircon refractive index is also very high (2.01), which is why this is typically used for producing white ceramic glazes.

The following crystalline phase, in a decreasing order of refractive indices, is sphene ($CaO{\cdot}TiO_2{\cdot}SiO_2$ refractive index: 1.91). Compositions bearing titanium tend to yellow.

Gahnite ($ZnO{\cdot}Al_2O_3$) has a refractive index of 1.8. The frits in which this phase devitrifies have high ZnO contents. This has been the subject of an as yet unpublished R&D project[4].

The other crystalline phases that can arise in greater or lesser proportions in ceramic glazes are wollastonite ($CaO{\cdot}SiO_2$), willemite ($ZnO{\cdot}SiO_2$), anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) and diopside ($CaO{\cdot}MgO{\cdot}2SiO_2$). The first three have refractive indices ranging from 1.58 to 1.63 and are usually found in matt glazes. Diopside has a refractive index of 1.67. This crystalline phase devitrifies quite readily and its proportion and size can be controlled by adjusting the CaO and MgO proportions

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[1]. FERNÁNDEZ NAVARRO, J.Mª. *El vidrio*. 2ª ed. Madrid: Consejo Superior de Investigaciones Científicas, 1991.
[2]. KLEIN, C.; HURLBUT, C.S. *Manual de mineralogía*. 4ª ed. Barcelona: Reverté, 1996.
[3]. NICKEL, E.H.; NICHOLS, M.C. *Mineral reference manual*. New York: Van Nostrand Reinhold, 1991.
[4]. *Obtaining smooth ceramic glazes with improved wear resistance and hardness*. EC RTD Project CR100191/BRE20395.

in the starting frit and the viscosity of the residual glassy phase at firing temperature.

2. MATERIALS AND EXPERIMENTAL TECHNIQUE

2.1. MATERIALS

Two standard industrial white floor tile glazes were used: a glossy (EB) and a matt glaze (EM), together with the solids mixtures required to produce the two glazes. Two frits were also used for this study, with the raw materials needed to produce them.

2.2. PROCEDURE

2.2.1. FRIT PREPARATION

The frits tested were obtained by fusing the corresponding raw materials mixtures in an electric laboratory kiln. Fusion temperature was 1500°C. The two selected frits were fused in a semi-industrial kiln.

2.2.2. SINTERING CURVES OF THE FRIT-KAOLIN MIXTURES

Frit-kaolin mixtures, in the particle sizes and proportions employed for wet applications to tile bodies (8g kaolin/100g frit), were used to determine the sintering curves. To do so, cylindrical test specimens were formed by pressing from these blends, which were then subjected to a non-isothermal heat-treatment cycle, ramping at a constant rate heating of 10°C/min in a hot-stage microscope. The sintering curve was obtained by measuring the evolution with temperature of test specimen size. This test was also run on the blends producing the glazes used as reference materials.

2.2.3. TEST SPECIMEN PREPARATION

Frit particle suspensions were prepared by mixing 100g frit with 8g kaolin, 0.2g sodium tripolyphosphate, 0.2g carboxymethylcellulose, and the necessary water to obtain a solids content of 70%. These mixtures were milled in a ball mill until a 2 wt% reject was obtained on a 40μm screen

The suspensions were applied to green floor tile bodies that had previously been engobed. The specimens were fired in an electric laboratory kiln at peak temperatures resembling those used industrially for this type of product.

The frits that were selected as most suitable were produced in a semi-industrial kiln, and were used to glaze industrial-size floor tile bodies, firing in a pilot roller kiln using an appropriate firing schedule for the body involved.

2.2.4. GLAZE CHARACTERISATION

The properties of the glazes obtained on a pilot scale were characterised and determined, as were those of the chosen reference glazes: glossy, white floor tile glaze (EB) and matt, white floor tile glaze (EM).

Glaze microstructure was examined by scanning electron microscopy (SEM), fitted with an energy dispersive X-ray microanalysis system (EDX). The crystalline phases present in the glazes were identified by X-ray diffraction (XRD).

2.2.4.1. CHROMATIC COORDINATES. HUNTER 60 WHITENESS INDEX. GLOSS

The chromatic coordinates and Hunter 60 whiteness index of the glaze surfaces were determined with a diffuse reflectance spectrophotometer. Measuring conditions were: standard CIE lighting and standard CIE 2° observer. Gloss was determined in a reflectometer, using a 60° light incident angle on the glaze surface. A minimum of five measurements was run, which were subsequently averaged.

2.2.4.2. MOHS HARDNESS. PEI. RESISTANCE TO WEAR BY ABRASION

Mohs scratch hardness (UNE 67-101) and abrasion resistance according to international standard ISO 10545-7 were determined.

Resistance to wear by abrasion (R_D) of the glazes was obtained by the PEI-based method[4] set out in standard EN 154. This is performed by subjecting the glaze surface to a certain number of revolutions in an abrasion tester, and then determining the surface profile in the abraded area with a roughness meter. Measurements were performed by a laser pick-up having a 1μm diameter. The profiles were measured with the roughness meter by diametrically traversing the abraded circle and also covering part of the original non-abraded surface at both points of the circle. The profile variations then allowed computing the cross section of the abraded area, which was then related with material volume loss in this area

Plotting material volume loss versus abrasion intensity, expressed as the number of revolutions in an abrasion tester, yields a straight line, the inverse of whose slope is taken as the resistance to wear by abrasion (R_D).

2.2.4.3. INNER POROSITY. APPARENT POROSITY. REVERSIBLE STAINING CAPACITY

Glaze inner porosity was determined in an image analyser hooked up to an optical microscope on polished cross-sectional slices of the glazes, by measuring the glaze surface fraction occupied by pores. The result was expressed as the percentage cross-sectional area of glaze occupied by pores

Glaze apparent porosity was estimated from the variation exhibited by chromatic coordinate L* of the glaze surface before staining with an indelible black felt-tip pen, and then after staining and cleaning of the surface with a cotton cloth moistened in alcohol until reaching constant L*.

2.2.4.4. RESISTANCE TO ACID AND ALKALI ATTACK

Glaze resistance to acid and alkali attack was determined according to standards ISO 10545-13 and UNE 67-122.

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[4]. *Obtaining smooth ceramic glazes with improved wear resistance and hardness.* EC RTD Project CR100191/BRE20395.

3. RESULTS

To compare the quality of the glossy and matt glazes developed from zirconium-free frits in the study, two commercial white glazes were selected as reference materials, whose characteristics were considered to be sufficiently representative of the standard properties of this type of coating: a matt zinc white glaze (EM) and a glossy zirconium white glaze (EB).

3.1. SINTERING CURVES OF THE RAW MATERIALS MIXTURES USED TO OBTAIN REFERENCE GLAZES EM AND EB

In order to establish the behaviour of the particle blends used to produce reference glazes EB and EM during heat treatment, their sintering curves were determined in a hot-stage microscope. The results have been plotted in Fig. 1.

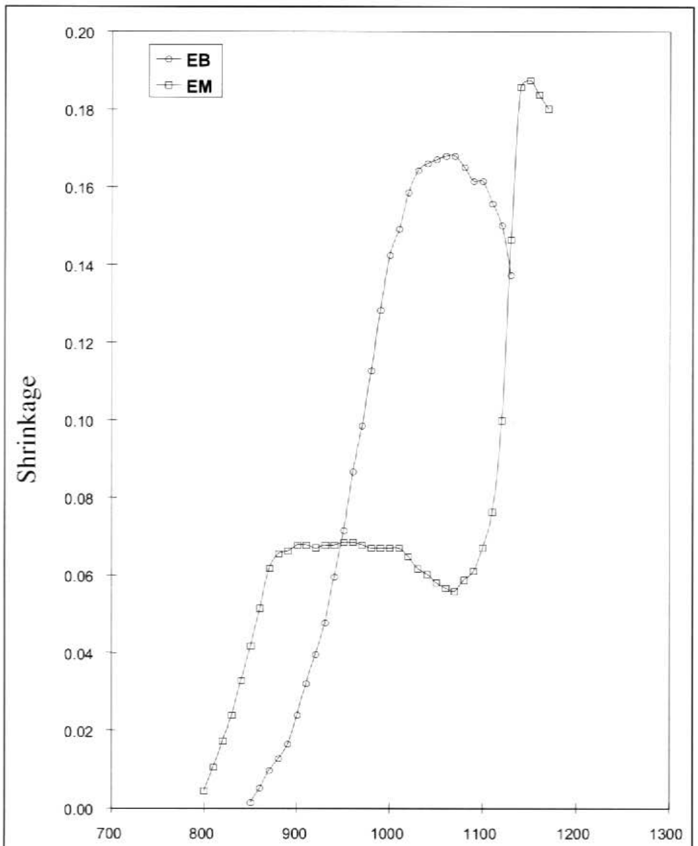

Figure 1. *Sintering curves of the blends producing the reference glazes.*

3.1.1. GLAZE EM

The curve of blend EM reveals that sintering started at 790°C. The densification rate rose with temperature up to 870°C, beyond which it decreased rapidly until cancelling out at 890°C. The horizontal stretch exhibited by these curves[6] coincided with devitrification of an important crystal proportion, which for this blend took place

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[6]. ESCARDINO, A. *Crystalline glazes*. In: IV World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1996, p. 87-110.

at relatively low temperatures. Crystal formation and growth gave rise to high viscosity in the melt, which momentarily impeded pore elimination, blocking specimen shrinkage.

Between approximately 1020 and 1060°C, the specimen expanded (linear shrinkage decreased), possibly owing to viscosity of the residual liquid phase decreasing enough to allow gases trapped in the remaining pores to expand or as a result of crystal growth. Sintering started again at 1060°C with high shrinkage, which could have been due to partial dissolution in the melt of previously formed crystals raising the quantity of liquid phase, which because of its decreasing viscosity allows pores to be eliminated.

At 1120°C, this specimens's shrinkage was still very low (≅13-14%). If it is borne in mind that temperature measuring systems in industrial kilns always show a reading around 15-20°C higher than electric laboratory kiln temperature measuring devices (to get the same result), this fact explains the relatively high sealed porosity found in Section 4.4.3 (Table 3) for glaze EM.

3.1.2. GLAZE EB

The blend that produced glaze EB started sintering at around 850°C. The curve exhibited a first stretch (850-900°C) with a lower slope, which progressively rose after 900°C.

In a DTA diagram of this blend, zircon devitrification was observed to arise in the 850-930°C range, with peak crystallisation rate occurring at 900°C. This circumstance explains the change in slope mentioned above. Thus, zircon would be devitrifying between 850 and 900°C [Section 3.3.2 (i)], while frit apparent viscosity kept relatively high, entailing slow shrinkage[6], [7]. After 900°C the crystal formation rate decreased. The curve developed an ever steeper slope for this reason and because viscosity of the residual glassy phase continued dropping as temperature rose, which led to a reduction in inner pores by viscous flow of this phase.

Maximum specimen densification (≅0.17) took place at 1030-1080°C, which is why the glaze produced by this blend at standard industrial kiln temperatures must exhibit low inner porosity

3.2. SINTERING CURVES OF THE SELECTED KAOLIN-FRIT BLENDS

3.2.1. SELECTED FRITS

The literature survey and availability of raw materials led to choosing the MgO-CaO-SiO_2 system as the base for formulating frits that would yield glossy and matt white glazes for floor tile bodies, using the typical firing schedules employed in industry for manufacturing this type of product.

Several frits were formulated in the diopside primary field, in view of the ternary

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[6]. ESCARDINO, A. *Crystalline glazes*. In: IV World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1996, p. 87-110.

[7]. AMORÓS, J.L.; ORTS, M.J.; GOZALBO, A., et al. *Evolution of glaze porosity in firing. Sintering mechanism and kinetics*. In: IV World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1996, p. 113-132.

diagram of the selected oxide system. Using these frits, the effect was studied of the percentage and type of other oxides (B_2O_3, alkaline earth oxides and ZnO) on sintering and crystallisation. The compositions that developed too much crystalline phase were rejected, since in order to form sufficient liquid phase to produce glossy glazes, crystals needed to dissolve, which occurred at much higher temperatures than the ones used in standard industrial firing cycles for floor tile manufacture. The compositions sealing at temperatures that were too low were also discarded, as they could produce pinholes in the resulting glaze.

Ultimately two promising frits were chosen from those prepared in the laboratory, which were based on the same oxide system (CaO-SiO_2-MgO), but had different compositions. These were fused in a semi-industrial kiln in order to run the tests set out in this study. One frit yielded a glossy and the other a semi-matt glaze hereinafter designated IB and IM respectively. The latter contained a greater proportion of CaO-MgO than the former.

3.2.2. SINTERING CURVES OF THE SELECTED KAOLIN-FRIT BLENDS. COMPARISON WITH THE CORRESPONDING CURVES OF SECTION 3.1.

3.2.2.1. GLAZE IM

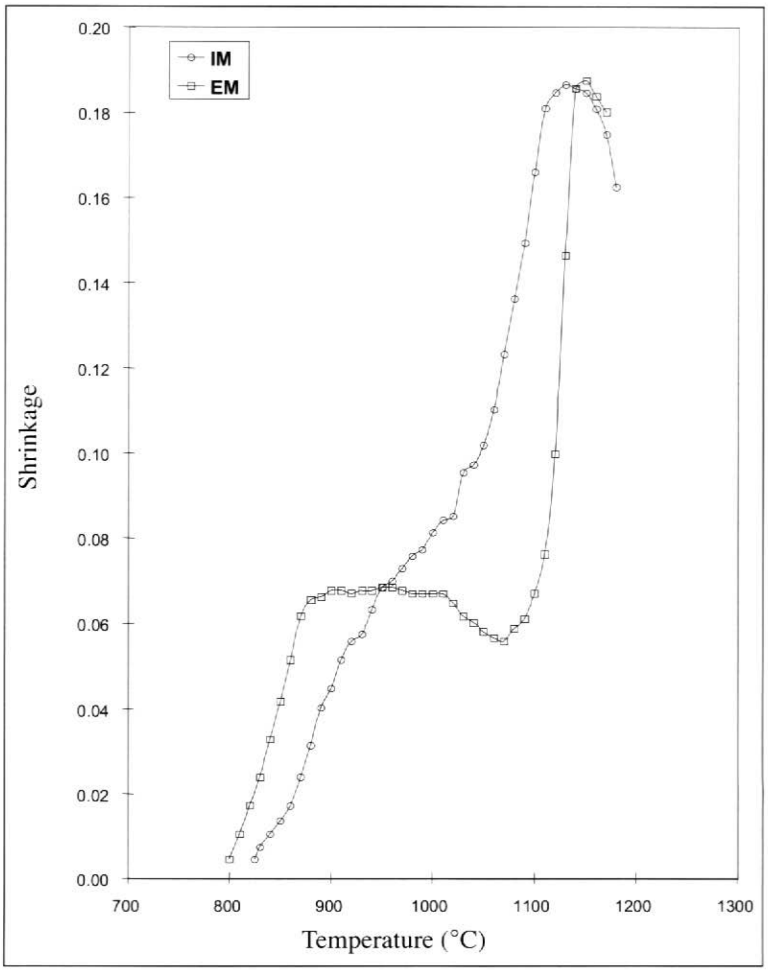

Figure 2. *Sintering curves of the blends producing matt glaze IM and reference glaze EM.*

Fig. 2 plots the sintering curves of kaolin-frit blend IM and reference blend EM

(Fig. 1). On comparing both plots, the IM blend was observed start sintering at higher temperatures (≅810°C) than the EM blend (≅790°C), which was beneficial as it encouraged the elimination of gases released by the body, which might cause pinholing. The sintering rate was relatively low between 850 and 1000°C, indicating that diopside crystals were forming and growing. This was subsequently verified by DTA. The sintering rate rose after 1050°C owing to the drop in residual liquid phase, which facilitated its access to the pores, and possibly also partially to formed crystals starting to dissolve.

Comparing specimen shrinkage at 1120°C in Fig. 2, a temperature that could roughly represent peak firing temperature in an industrial schedule, allows inferring that in glaze IM the viscosity of the glassy phase was lower than that of glaze EM (IM shrinkage was 0.19; in EM this was 0.13), so that the former should in principle be glossier and less porous than the latter.

3.2.2.2. GLAZE IB

The sintering curves of the blends that yielded glossy glaze IB developed in the study and reference glaze EB have been plotted in Fig. 3. It can be observed that up to around 925°C, both mixtures exhibited similar behaviour. Beyond this temperature, up to about 1025°C blend IB sintered at a much slower rate than blend EB owing to the start of diopside crystallisation in this region. Zircon crystallisation, the crystalline phase devitrifying in frit EB, developed between 850 and 930°C as indicated previously (Section 3.1.2). Moreover, EB maximum shrinkage took place at lower temperatures than that of IB.

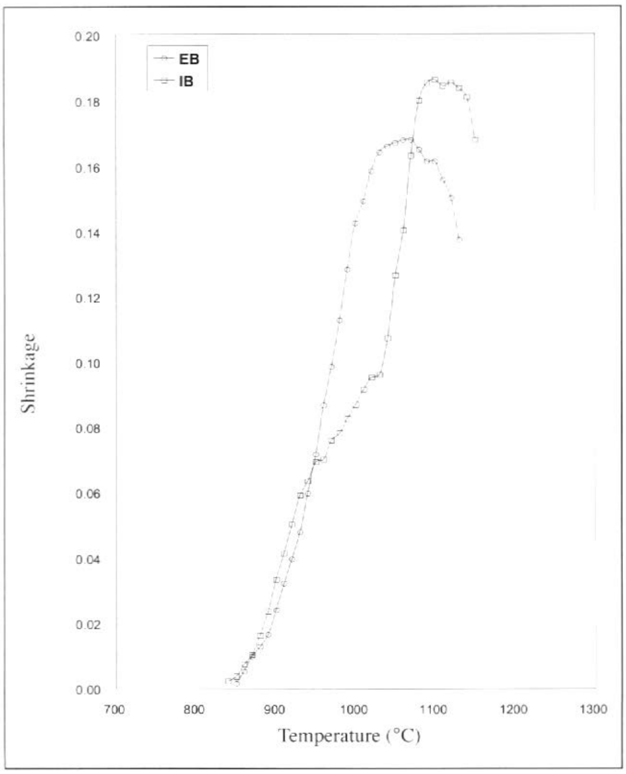

Figure 3. Sintering curves of the blends producing glossy glaze IB and reference glaze EB.

3.3. SEM, EDX AND XRD STUDIES OF THE CRYSTALLINE PHASES PRESENT IN REFERENCE GLAZES EM AND EB, AND IN GLAZES IM AND IB PRODUCED WITH THE SELECTED FRITS

A scanning electron microscope (SEM) fitted with EDX was used to examine glaze microstructure and determine the presence of the major chemical elements present in the polished cross sections of the glaze coatings obtained with the four starting raw materials blends (EM, EB, IM and IB). The crystalline phases present were identified by X-ray diffraction in the fired test specimens using the same heat-treatment schedule as the one employed in industry for manufacturing glazed floor tiles. The test specimens were formed by casting from aqueous suspensions of the above starting mixtures.

3.3.1. MATT GLAZES

i) Glaze EM.

The microphotographs of Figs. 4 and 5 correspond to the polished cross section of glaze EM. They show some glossy, needle-like crystals, up to 10μm long, made of Si/Zn, as well as other needle-like crystals, darker than the glassy matrix, up to 6μm long, made of Al/Si/Ca. Zircon, quartz and corundum particles can also be observed, which were part of the starting solids blend and did not melt in firing. Zircon has a particle size of less than 5μm. Quartz mean particle size is 15-20μm, and quartz particle edges are partly rounded, indicating partial dissolution in the melt during firing. It deserves pointing out that pores were found beside many quartz particles, which may be due to partial dissolution of these particles producing highly viscous glass (rich in silica), in which bubbles were trapped. Finally, alumina particles sized 5-10μm can be observed surrounded by a layer about 0.5μm thick, which was lighter in colour than the rest of the particle. EDX analysis of this region revealed that it consisted of Al/Zn.

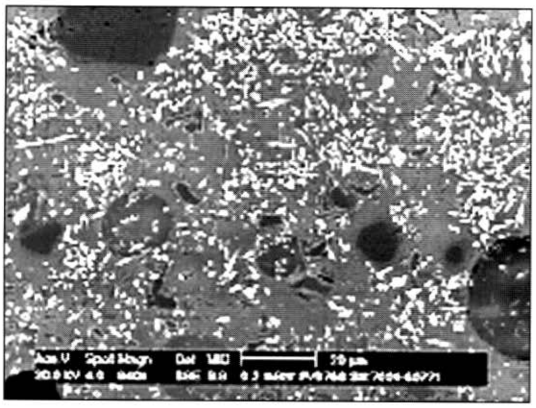

Figure 4. *Cross section of glaze EM.*

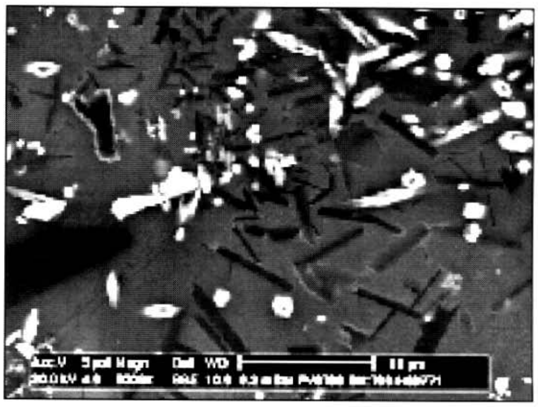

Figure 5. *Cross section of glaze EM.*

The crystalline phases identified by XRD in this glaze were: willemite

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[8]. FELIU, C. *Estudio cinético de la desvitrificación de diópsido en fritas basadas en el sistema de óxidos SiO_2-MgO-CaO*. Castellón : Universitat Jaume I, Chemical Engineering Department 1996. Doctoral dissertation.

[9]. OMAR, A.A.; SALMAN, S.M.; MAHMOUD, M.Y. *Phase relations in the Diopside-Anorthite-Akermanite system*. Ceram. Int., 12, 53-59, 1996.

($2ZnO.SiO_2$), anorthite ($CaO.Al_2O_3.2SiO_2$), zircon ($ZrSiO_4$), quartz (SiO_2) and corundum (Al_2O_3). No crystalline phase was detected of composition Al/Zn, which corresponded to the layer surrounding the corundum particles, probably because of their low concentration in the tested sample or because a solid solution of Zn inside the alumina was involved.

ii) Glaze IM.

The appearance of glaze IM can be appreciated in Figs. 6 and 7. In this glaze, crystals of 1 to 5μm can be observed, uniformly distributed in the glassy matrix. XRD revealed that diopside crystals ($MgO{\cdot}CaO{\cdot}2SiO_2$) were involved. Fig. 6 shows crystal-free areas of 10 to 30μm, because the diopside crystallised at the surface[8], [9] and, since the heat-treatment cycle was fast, crystals did not form inside the larger starting frit particles.

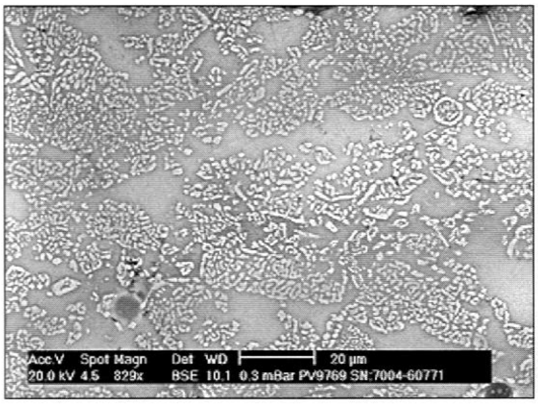

Figure 6. *Cross section of glaze IM.*

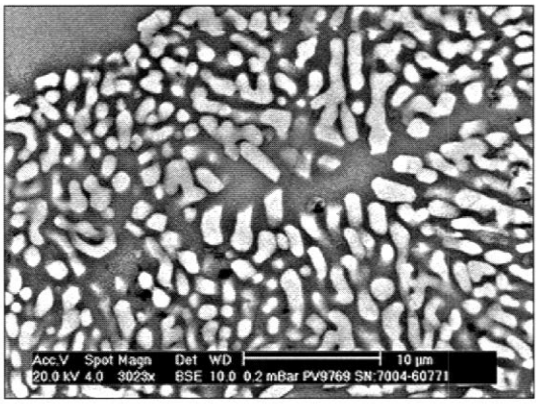

Figure 7. *Cross section of glaze IM.*

3.3.2. GLOSSY GLAZES

i) Glaze EB.

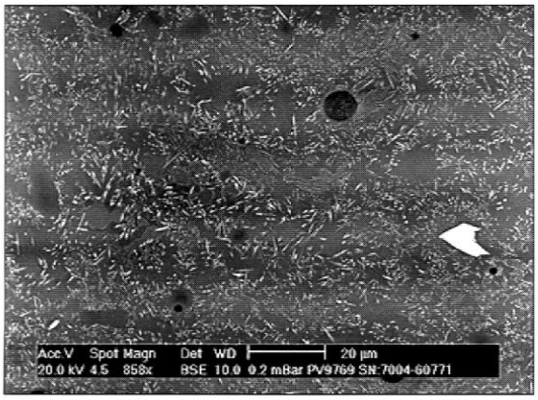

Figure 8. *Glaze EB cross section.*

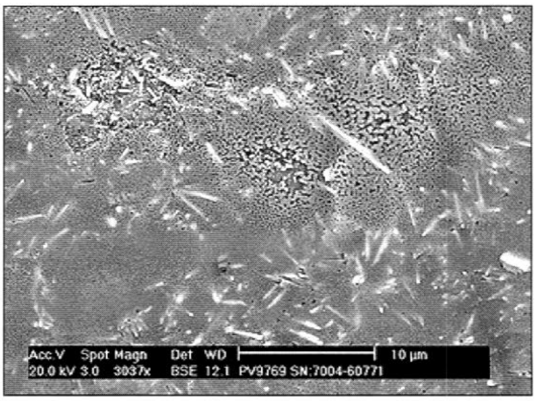

Figure 9. *Glaze EB cross section.*

Zircon was the sole crystalline phase present in reference glossy glaze EB. SEM observation (Figs. 8 and 9) revealed needle-like zirconium silicate crystals of up to 0.5 x 7 μm, together with some unmelted zircon particles from the starting frit. These unmelted particles had an irregular shape, were of the same colour as the needle-like crystals, and were larger. Zircon crystals were found dispersed in a glassy matrix that exhibited immiscible-liquid-phase separation (Fig. 9. In this glaze, crystal-free areas can also be observed, owing to zircon crystallisation preferentially occurring from the surface of the original frit particles inwards[10].

ii) Glaze IB.

The micrographs of Figs. 10 and 11 correspond to glossy glaze IB developed in the study. Its appearance was similar to that of matt glaze IM, the difference being that in IB a smaller proportion of crystalline phase was observed, and the diopside crystals were smaller (0.5-1μm) than those observed in IM.

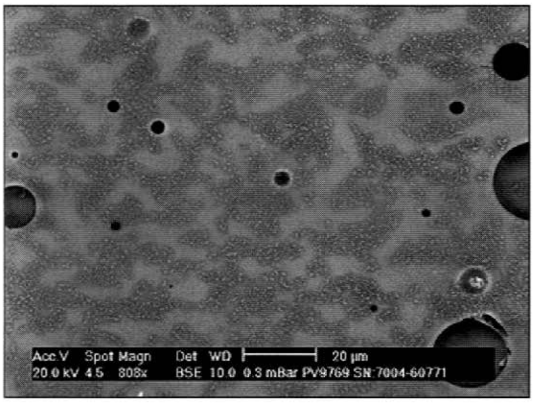

Figure 10. *Cross section of glaze IB.*

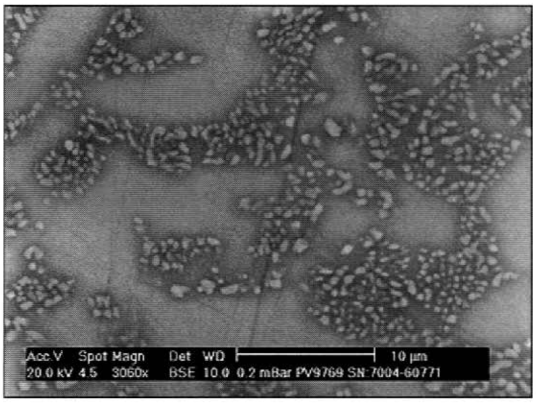

Figure 11. *Cross section of glaze IB.*

3.4. PROPERTIES OF THE REFERENCE GLAZE COATINGS AND THOSE OBTAINED FROM THE SELECTED FRITS

3.4.1. CHROMATIC COORDINATES, HUNTER WHITENESS INDEX, GLOSS

Table 1 details the optical characteristics determined at the glaze surfaces of the specimens fired in the pilot roller kiln. In the matt glazes, the whiteness index and gloss of glaze IM were higher than those of glaze EM. The difference in gloss between these glazes can be associated with the difference in size of the crystalline phases that they contain. Thus, comparing Figs. 5 and 7 reveals that the diopside crystals in glaze IM (Fig. 7) were smaller than those of anorthite, willemite, quartz, corundum and zircon in glaze EM (Fig. 5).

With regard to the glossy glazes, the gloss values were found to be similar (slightly higher in glaze IB), however the whiteness index of glaze EB was a little higher than that of IB. The whiteness index depends on chromatic coordinates L* and b*, the higher the value of L* and the lower that of b*, the higher is the whiteness index. The value of L* in glaze EB was only two points higher than that of glaze IB, but the difference in coordinate b* values (that of glaze EB was negative) produced a greater difference in the Hunter whiteness index value. The fact that chromatic coordinate b* was negative for this glaze,

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[10]. MORENO, A. *Estudio de la formación de fases cristalinas en vidriados blancos de circonio: factores que influyen sobre su índice de blancura.* Castellón: Universitat Jaume I, Chemical Engineering Department, 1994. Doctoral dissertation.

i. e. it had a slight blue component, was in all likelihood due to the glassy-phase separation observed in Fig. 9[11].

Glaze	L*	a*	b*	Hunter 60 whiteness	Gloss (60°)
EM	87.17	-0.63	0.95	81.1	40.7
IM	88.01	-0.57	0.44	83.6	50.8
EB	90.51	-0.65	-0.35	89.1	86.7
IB	88.62	-0.73	0.98	82.8	88.1

Table 1. *Chromatic coordinates, whiteness and gloss for glazes IM and IB developed in the study and reference glazes EM and EB.*

The differences in whiteness and gloss between glazes IM and IB were due to the structural differences described in Section 3.3, since glaze IM contained more diopside crystals (greater whiteness) of larger size (less gloss) than glaze IB.

3.4.2. MOHS HARDNESS, RESISTANCE TO WEAR BY ABRASION, PEI

Table 2 details the values for Mohs scratch hardness, resistance to wear by abrasion (determined by mass loss with a roughness meter[5]), and abrasion resistance according to standard ISO 10545-7.

It can be observed that matt glaze IM obtained from the selected frit exhibited higher Mohs hardness than reference matt glaze EM. It also exhibited greater resistance to wear by abrasion, since the resistance to wear (R_D) of glaze IM was more than twice that of glaze EM. The same was the case with the number of revolutions needed before visible failure was found at the surface (standard ISO-10545-7), which signified an important improvement in PEI.

As far as the glossy glazes were concerned, Mohs hardness[3] and the values of RD and PEI were of the same order (about 2000 and class 5, respectively).

Glaze	Mohs	Resistance to wear by abrasion (R_D) (rev.µm/µm^2)	Abrasion resistance (ISO-10545-7)	
			Visible stage (rev.)	Class
EM	4	1000	6000	4
IM	5	2200	>12000	5
EB	3	1600	>12000	5
IB	3	2000	>12000	5

Table 2. *Scratch hardness, resistance to wear by abrasion and abrasion resistance of glazes IM and IB developed in the study, and of reference glazes EM and EB.*

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[3]. NICKEL, E.H.; NICHOLS, M.C. *Mineral reference manual.* New York: Van Nostrand Reinhold, 1991.

[5]. IBÁÑEZ, M.J.; ESCARDINO, A.; LEMUS, R. de, et al. *Variation of roughness and gloss in glazed tile with the intensity of the wear produced in a standard abrasion tester.* In: IV World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1996, p. 727-729.

[11]. APARICI, J.; NUÑEZ, M.V.; MORENO, A., et al. *Liquid-phase separation in glazes for porous single-fired wall tile.* In: II World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1992, p. 245-262.

3.4.3. SEALED AND APPARENT POROSITY

Irreversible stain retention in a glaze is directly related to the number of open pores at the glaze surface. It was therefore vital to determine whether the studied glazes, both those used as models as well as those developed in the study, possessed surface pores. It was furthermore essential to determine the sealed porosity or bubble percentage in the glazes, since this was related to potential irreversible stain retention capacity with wear in service.

With regard to apparent surface porosity, on running the test described in Section 2.2.4.3 only a very slight difference was detected ($\Delta L^*=0.25$) between coordinate L* of the surface prior to staining and of the clean surface (after staining) in the case of glaze EM. In the other three glazes, the values of ΔL^* were negligible (fluctuating between 0.04 for IM and 0.01 for EB). It should be pointed out that at $\Delta L^* = 0.25$, no staining is visually detected. A stereoscopic microscope needs to be used to find micropores that have absorbed black ink from the felt-tipped pen.

Table 3 reports the values obtained for sealed porosity, expressed as the percentage of the glaze cross-section occupied by pores (bubbles). In this case as well, glaze IM exhibited better characteristics than reference glaze EM. In fact, the sealed porosity of glaze EM (11.5%) was practically twice that of IM (5.8%). This can be visually appreciated on comparing Figs. 12 and 13.

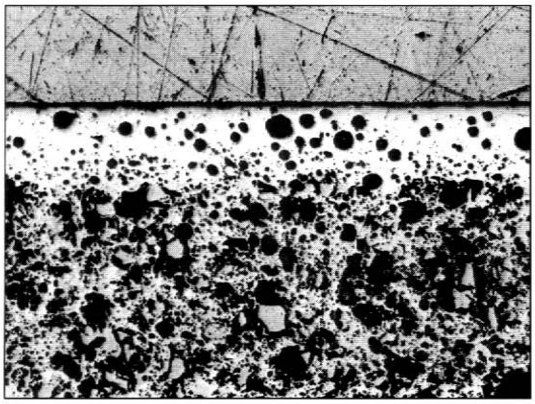

Figure 12. *Polished cross section of glaze EM.*

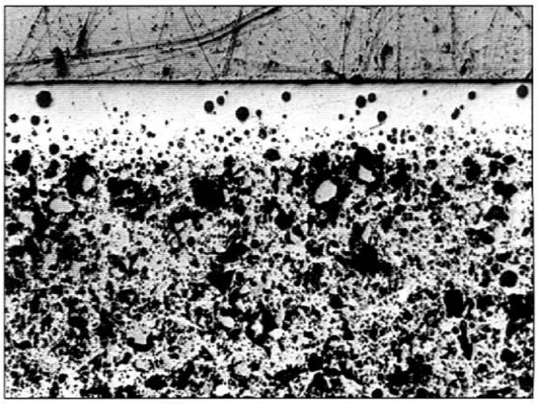

Figure 13. *Polished cross section of glaze IM.*

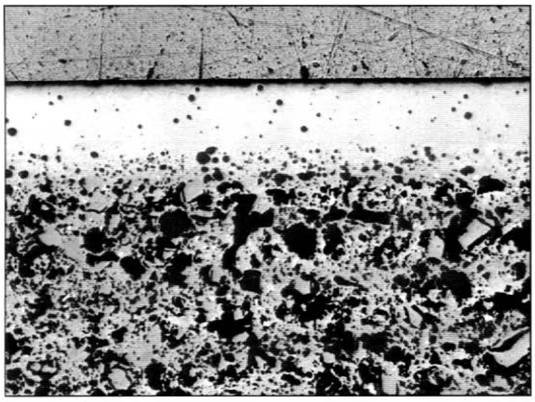

Figure 14. *Polished cross section of glaze EB.*

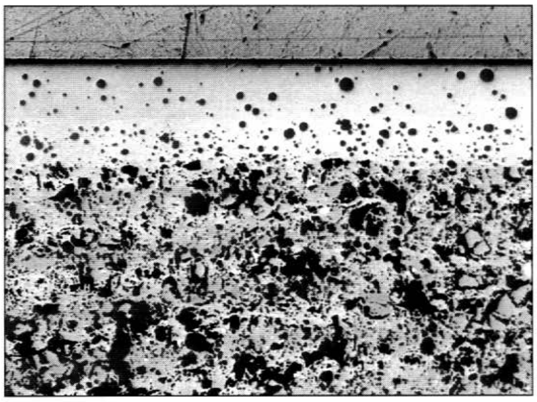

Figure 15. *Polished cross section of glaze IB.*

As regards the glossy glazes, the sealed porosity of glaze IB (3.7%) presented a very good value (see Fig. 15) for a floor tile glaze, since in industrial production such glazes usually exhibit sealed porosities ranging from 3.7 to 8.0%, except for the ones obtained only from a zirconium frit and kaolin (glaze EB), which have an inner porosity in the range 1.3 to 1.7% (Table 3), which is very small, as the photograph in Fig. 14 shows. (The four photographs in Figs. 11 to 14 were taken using the same magnification.)

Glaze	Sealed porosity (% sectional area occupied by pores)	Resistance to chemical agents		
		UNE-67-122-85		ISO 10545-13
		HCl	KOH	
EM	11.5	B	A	GLB
IM	5.8	AA	A	GLA
EB	1.7	AA	AA	GLA
IB	3.7	AA	A	GLA

Table 3. *Sealed porosity and resistance to chemical agents of glazes IM and IB developed in the study and reference glazes EM and EB*

3.4.4. RESISTANCE TO ACID AND ALKALI ATTACK

The results obtained on applying the tests set out in standards UNE 67-122-85 and ISO 10545-13 have been listed in Table 3.

It can be observed that matt glaze IM obtained from the frit developed in the study exhibited greater resistance to acid attack and a better response to standard ISO 10545-13 than glaze EM which served as a model.

Glaze IB exhibited analogous resistance to HCl attack and identical behaviour on applying the ISO standard as reference glaze EB, and was slightly more sensitive to alkali attack though the rating obtained (A) lay within admissible limits.

4. CONCLUSIONS

4.1. Two zirconium-free frits with different compositions were obtained in a semi-industrial kiln, based on the oxide system MgO-SiO_2-CaO, which on being mixed with 8% kaolin by weight yielded a matt white (IM) and glossy white (IB) glaze for glazed floor tile manufacture.

4.2. Morphological analysis (SEM), with EDX and XRD showed that diopside was the devitrifying crystalline phase responsible for the opacity and whiteness of both resulting glazes (IB and IM).

4.3. The whiteness index, gloss, apparent and sealed porosity, Mohs hardness, resistance to wear by abrasion and resistance to chemical attack (acids and alkalis) were better in matt glaze IM developed in the study than reference glaze EM, which was a matt zinc white glaze.

4.4. Glossy glaze IB developed in the study was slightly glossier than the reference glossy white glaze (obtained from a zirconium frit), exhibited a slightly lower whiteness index, identical Mohs hardness and the same resistance to wear by abrasion. Glaze IB had a slightly higher inner porosity although lower or of the same order as most commercially available floor tile glazes, and a resistance to chemical agents comparable to that of the reference glossy glaze used in the study.