AVOIDING WATER MARK FORMATION BY ADJUSTING ENGOBE LAYER CHARACTERISTICS

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ABSTRACT

The water mark, a relatively common phenomenon in ceramic tiles, consists of an alteration of the aesthetic properties of the glazed tile surface when the body becomes wet. Given the great number of claims made because of this type of problem by ceramic tile consumers in Brazil, the objective of this study has been to contribute to minimising the problem by studying the effect of the engobe composition on the water mark in single fire porous tiles. The evaluation of the results consisted of measuring changes in colour of the glazed tile surfaces by a colorimeter, after preset periods of water immersion. Besides contributing to a better understanding of the phenomenon, the results indicate that the engobe composition plays a key role in the development of the water mark and that its occurrence can be avoided by appropriate engobe formulation.

1. INTRODUCTION

The term water mark is used to describe "darkening" of the glazed ceramic tile surface, when the porous tile body absorbs water. When this phenomenon appears with already installed tiles, the alteration of the tile colour adversely affects the aesthetic characteristics of the environment. Water can enter into contact with ceramic tiles in different ways:

- mortar used in the fixing;
- intentional wetting of the tiles before fixing;
- water present in the external environment, which can enter through the joint;
- pipe leaks in internal building structures;
- moisture from walls with inadequate waterproofing;
- tile exposure to moist environments before fixing.

Water marks are currently the main source of claims and lawsuits involving tiles certified in Brazil. An initial analysis carried out by the Ceramic Centre of Brazil (CCB) - organisation responsible for ceramic tile certification in the country – indicated that of 496 certified products made by different manufacturers, approximately 40% of these presented water marks. It is important to point out that the great majority of Brazilian consumers seeks glossy, transparent products, where water marks are much more likely to appear.

The results of statistical analysis of the data collected by CCB are presented in Figure 1. It can be observed that water marks preferentially occur in products with high apparent porosity, particularly in semi-porous and porous tiles.

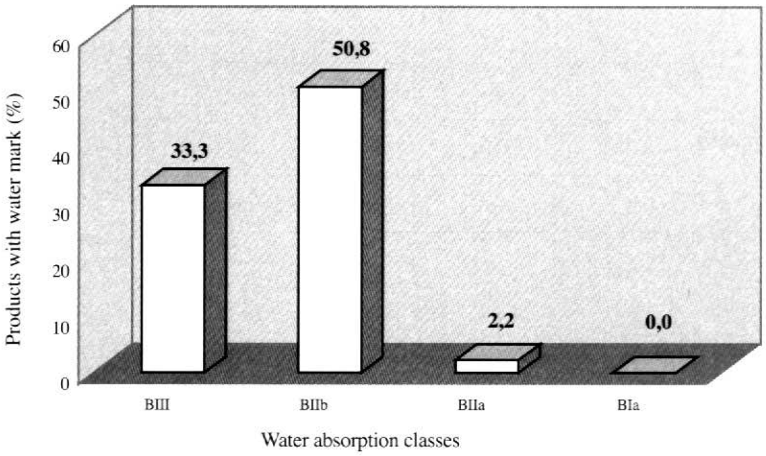


Figure 1. Effect of the absorption class on the appearance of the water mark.

In order to effectively eliminate the problem, or at least control it, it is necessary to understand its origin. The evidence suggests that the origin of the water mark is related to the visualisation, through the glazed surface, of the alteration of the visual appearance of the porous body on becoming wet. Therefore water marks only occur when the combined opacity[1] of the glaze/engobe has not been sufficient to impede visualising the change in "colour" of the body. Thus, considering that the glaze will continue to be transparent and the body porous, the only feasible alternative for solving the problem is by controlling the opacity of the engobe[2]. Engobe opacity can be considered to depend fundamentally on three parameters: 1) thickness of the layer; 2) transparency of the solid phase and 3) presence of open pores. Points 1 and 2 are self-explanatory but the effect of porosity deserves to be analysed in more detail.

Briefly, with regard to the issue at point, the key feature is to understand the difference between what happens when the pores are full of air or water. It is well known that part of the incident light on an interface between two transparent media, depending on the angle of incidence and difference between the refractive indexes, can undergo a process known as total internal reflection (TIR). The conditions in which TIR occurs are found from the following equation:

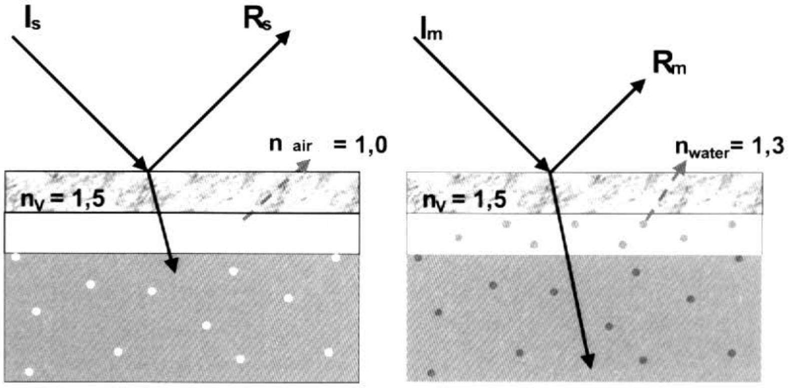
$$\text{sen}\ \theta_c = n_2/n_1 \qquad [1]$$

Where θ_c is the critical angle from which TIR is given (angles of incidence larger than θ_c will undergo TIR) and n_1 and n_2 correspond respectively to the refractive indexes of the media from which the light comes and through which it passes. As consequence of the TIR phenomenon, part of the incident light does not penetrate inside the pore. Considering $n_{glaze} = 1.5$, $n_{air} = 1.0$ and $n_{water} = 1.3$, it can be concluded from equation [1] that the critical angles of incidence (θ_c) for pores filled with air and water are 41.8° and 50.3°, respectively, i.e., the rays of light whose angles of incidence on the glaze/pore interface are larger than these values will undergo total internal reflection (TIR) and not penetrate inside the pores. Thus the quantity of light that penetrates inside the pores of the engobe is larger when these are filled with water than with air. Therefore, as the engobe is porous, when the pores are filled with water, they become more transparent than when they are filled with air.

Another way of approaching the problem is by evaluating the fraction of incident light (I_E) that would be reflected (I_R) by an interface between two materials with different refractive indexes (n_0 and n_v), according to the equation [2].

$$I_R = \frac{I_E(n_o - n_v)^2}{(n_o + n_v)^2} \qquad [2]$$

Using the refractive indexes given previously, the conclusion is reached that the intensities of reflected light (I_R) for the air/glass and water/glass interfaces would be 0.04 and 0.0051 respectively, as illustrated in Figure 2.



Dry Tile

Wet Tile

Figure 2 – Illustration of loss of opacity by the porous engobes after wetting.

This preliminary analysis indicates that from the point of view of the engobe, there are basically three alternatives for addressing the problem of water marks: 1) increasing the thickness of the layer; 2) increasing the opacity of the solid phase and 3) eliminating open pores. These alternatives could be used separately or simultaneously. It is to be noted that, in relation to other aspects, it is more convenient and therefore more practical for manufacturers to use porous engobes.

Other alternatives, not related directly to the engobe, would be: 1) reducing porosity of the body and 2) increasing glaze opacity.

Engobe layer thickness is controlled by adjusting application conditions, and as it is economically feasible and does not affect other characteristics, this can be easily done.

The solid (non-porous) phase of the engobe usually consists of a glassy matrix (amorphous) and crystalline phases. The opacity of this set of materials depends on the differences between the refractive indexes of the glassy matrix and the crystals[3]. As shown in equation 2, the greater this difference, the greater will be the opacity of the set of materials. Crystals can be added to the engobe formula or form during firing. At present, zirconium silicate is the most widely used opacifier owing to its high refractive index (1.94) and high refractoriness, which is a fundamental requirement so that the crystals do not dissolve in the glassy matrix during firing. Table I presents the refractive indexes of some materials.

Materials	n
Glass	1.50
Mullite	1.65
Alumina	1.76
Zirconium silicate	1.94
Air	1.00
Water	1.30

Table I. Refractive indexes (n) of some materials.

Open pores can be eliminated by increasing engobe meltability. The fluxes used in the engobe formulas can be divided into primary and secondary fluxes[4]. In the primary fluxes, white frits are the most noteworthy, which soften at temperatures lower than 800°C and start the dissolving process of the most refractory components. Raw materials with a low melting point or their eutectic combinations are used as secondary fluxes. Feldspars, talc and the raw materials that contribute alkaline and/or alkaline-earth elements are found in this group.

2. OBJECTIVE

The objective of the present work has been to establish the main aspects to be considered in defining the engobe composition that would enable eliminating water marks in porous ceramic tiles with transparent glazes manufactured by single firing.

3. EXPERIMENTAL PROCEDURE

The experimental procedure adopted was divided into two stages. The objective of the first stage was to develop a simple and effective tool for quantitatively evaluating the formation and disappearance of water marks. Using the methodology developed in the first stage and the analysis set out in the introduction, the objective of the second stage was to study the effects of the following variables: 1) layer thickness; 2) transparency of the solid phase and 3) presence of open pores.

An interesting feature of the methodology used is its contribution to a better understanding of the role of the engobe which, though found in almost all porous tiles, has till today practically never been systematically studied in depth.

3.1. QUANTIFICATION OF THE WATER MARK

Although the few works published[5] on water marks suggest the use of colorimetric techniques to measure the intensity of the variation in colour presented by the tiles on absorbing water, none go into further details concerning this possibility. In view of this, it was decided to develop a methodology based on this suggestion. Taking into account the above remarks, it was decided to characterise the phenomenon by evaluating three fundamental aspects: 1) water mark formation rate, 2) maximum intensity after a certain period of water immersion and 3) water mark disappearance rate.

The adopted experimental procedure is schematically presented in Figure 3. Initially a reading was made using the three colour co-ordinates of three dry tile regions, with a portable colorimeter (Minolta model CM-508-d). The three measurement points were defined by means of a template to ensure that after water immersion, the readings would be made at the same points. Having made the three readings the mean values of the co-ordinates[4,6], L^*, a^* and b^*, supplied by the colorimeter in each reading, were calculated. After water immersion for preset times, the glazed surfaces were dried with a dry cloth and the colorimetric readings were performed at the same points as before on the dry tiles. The measured colour variations found in the tiles before and after water immersion were evaluated by means of the parameter ΔE^*, which allowed quantifying the intensity of the arising stains.

To evaluate the disappearance of the water mark a similar procedure was adopted, the only difference being that the periods of time between one colorimetric measurement and the next one, now corresponded to drying time in air.

In the study conducted, measurements were made on the tiles after every 5 minutes' immersion, seeking to determine the kinetics of mark formation. After an hour's water immersion, the tile was set to dry in a ventilated environment, keeping the faces exposed to air. Colorimetric measurements were periodically carried out on the tile, always at the three points initially established with a template, with the intention of evaluating mark disappearance.

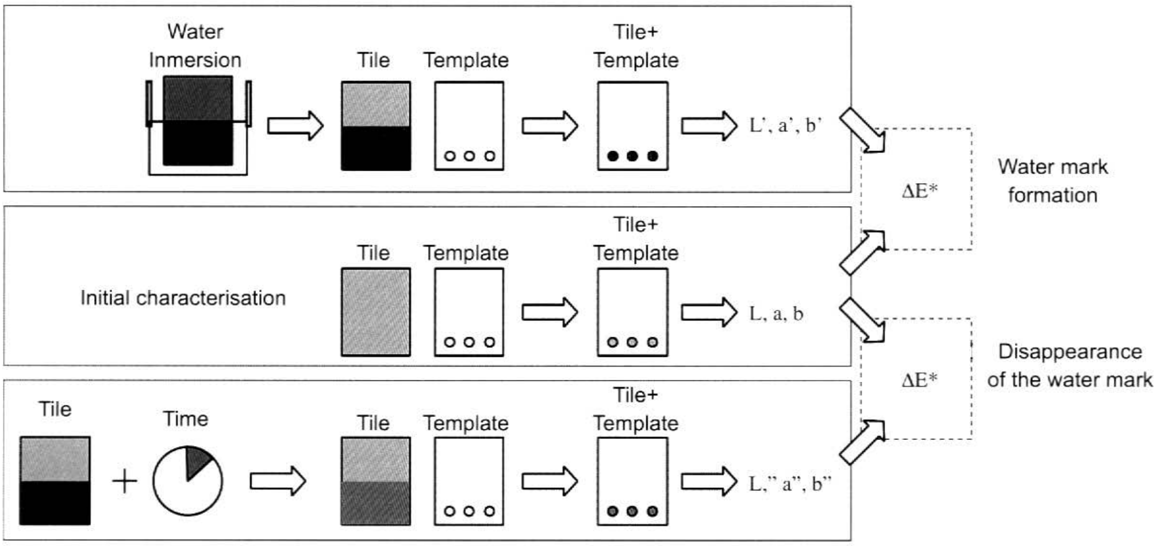


Figure 3. Schematic illustration of the procedure used to evaluate the water mark.

3.2. STUDY OF THE VARIABLES THAT AFFECT WATER MARK FORMATION

First the effect of varying engobe layer thickness was evaluated. In this part of the study a standard engobe was used for monoporosa products that presented a high tendency to form water marks. The engobe was milled in a fast laboratory mill until reaching a reject between 0.5 and 1.0%, in an ABNT #325 sieve (aperture of 44 μm). Subsequently, engobe layers were applied of 40, 50, 60, 70 and 80 g on porous industrial tiles of nominal dimensions 30 x 40 cm. Such applications correspond to specific layers of 330, 420, 500, 580 and 670 g wet engobe/m^2 tile. The tiles were glazed and fired in an industrial kiln at 1120°C in a 45 min cycle. Tile water absorption after the firing was approximately 15.0%.

To evaluate the effects of the engobe composition on water marks, several formulas were developed, using different raw materials in varying proportions. Initially two engobes were used. The first, called standard engobe (P) is mentioned in the literature as a typical example of a porous wall tile engobe. The second was developed from the standard engobe (P), reducing the refractory raw materials content and raising flux content. As this composition is more fluxing it is referenced F. Table II sets out the compositions of P and F

Raw materials (%)	P	F
Argentina clay	18.0	12.0
Kaolin	6.0	3.0
Bentonite	0.4	0.4
Quartz	18.0	10.0
Sodium feldspar	19.6	36.6
White frit	20.0	20.0
Zirconium silicate #500	18.0	18.0
Tetrasodium pyrophosphate	0.4	0.4
CMC	0.2	0.2

Table II. Engobe compositions used in the first part of the study.

Based on the more fluxing composition (F), others were developed that allowed us to study separately the influence of each raw material on the characteristics of the engobe. The effects of the following changes in the composition of this engobe were evaluated:

- Nature of the clay;
- Zirconium silicate particle size and content;
- Content of the raw materials that contribute alkaline-earth oxides (talc, diopside and wollastonite);
- Nature and content of the feldspars (orthoclase, albite and spodumene);
- Frit content.

In this stage of the study, processing conditions were kept steady. Engobe reject was held between 0.5 and 1.0% on an ABNT #325 sieve (44 μm), while engobe and glaze layer application was controlled in terms of the applied weight, at 625 g engobe/m^2 and 735 g glaze/m^2. Firing was conducted under the same conditions described previously.

The glaze used was always the same one, unless explicitly changed, and corresponds to an industrial single-fire glaze essentially consisting of frits and suspending agents. In the final stage of the work the effects of the following modification in its chemical composition were evaluated:

- Substitution of the transparent glaze by an opaque glaze;
- Addition of different white frit contents to the standard glaze;
- Addition of different zirconium silicate contents to the standard glaze.

All the tests carried out were analysed quantitatively regarding water mark formation and disappearance by colorimetry, in accordance with the procedures set out in point 2.1.

4. RESULTS AND DISCUSSION

4.1. QUANTITATIVE EVALUATION OF THE WATER MARK

Figure 4 plots the evolution of the water mark with water immersion time and the disappearance of the water mark during tile drying. The curve shows that the intensity of the stain increases quickly at the beginning and later tends to stabilise. Tile staining develops practically during the first five minutes of immersion and then exhibits a low rate of growth. During drying, the mark is observed to disappear gradually, presenting a slightly higher drying rate at drying start. The time required for the elimination of the stain was considerably longer than the time needed for it to form. Analysis of these results indicates that the developed methodology enables quantitative evaluation of the evolution of stain intensity across time and is shown to be appropriate for the purposes of the present work. The generally used visual evaluations only permit comparative assessments.

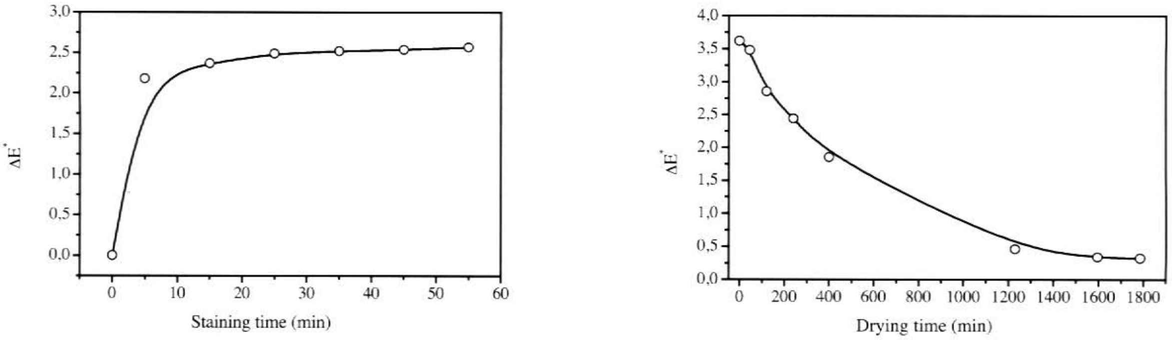


Figure 4. Variation of stain intensity (ΔE^*) with time.

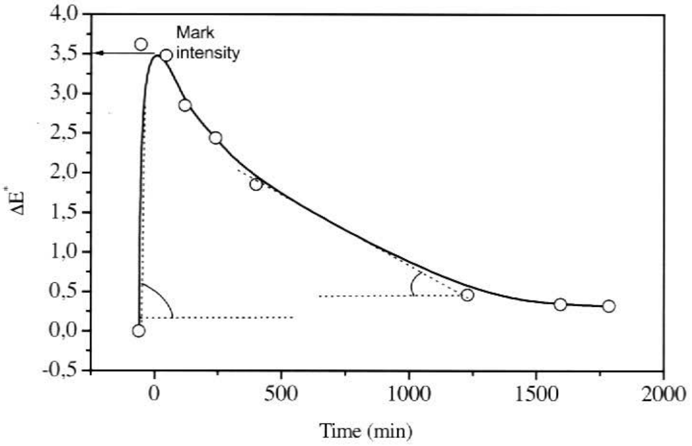


Figure 5. Staining curve of an industrial tile with the formation of a high intensity water mark.

Combining the curves of water mark formation and disappearance generates the staining curve (Figure 5). The maximum point of the curve represents the maximum intensity of the mark after water immersion time. The curve slopes in the staining and drying stages respectively indicate the staining and disappearance rates.

Analysis of the results found in the later phases of the work confirmed the existence of a direct relation between mark intensity at the end of the water immersion time and its intensity after 3 hour drying (Figure 6). This result indicates that for a body made from the same composition, under the same processing conditions, water mark drying rate does not alter very much, independently of the engobe and glaze used. Therefore, the results set out below only take into consideration the intensity of the mark formed after 30 min immersion.

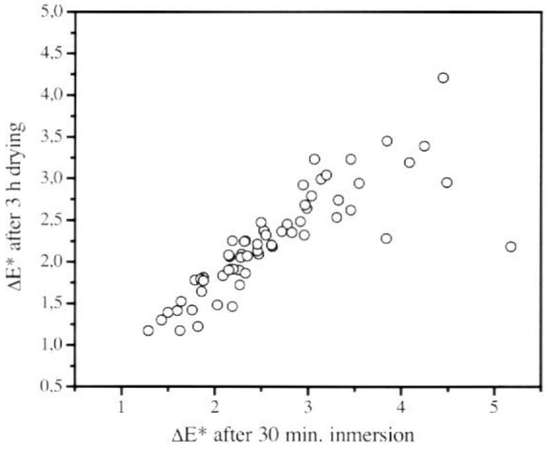


Figure 6. Relation between maximum water mark intensity and intensity after 3 hour drying.

4.2. STUDY OF THE VARIABLES THAT AFFECT WATER MARK FORMATION

4.2.1 Engobe layer thickness

Figure 7 simultaneously plots the staining curves of the tiles made with different engobe layer thicknesses, as well as the relation between water mark intensity and applied layer weight. As mentioned previously, the staining and mark disappearance rates did not undergo significant alterations among the compositions. However, maximum mark intensity was noticeably affected by the variation of engobe layer thickness.

Figure 7 shows that the tiles made with thicker engobe layers presented less intense marks than the others. This result indicates that the thickness of the engobe layer can be an important variable in avoiding water mark formation in porous tiles.

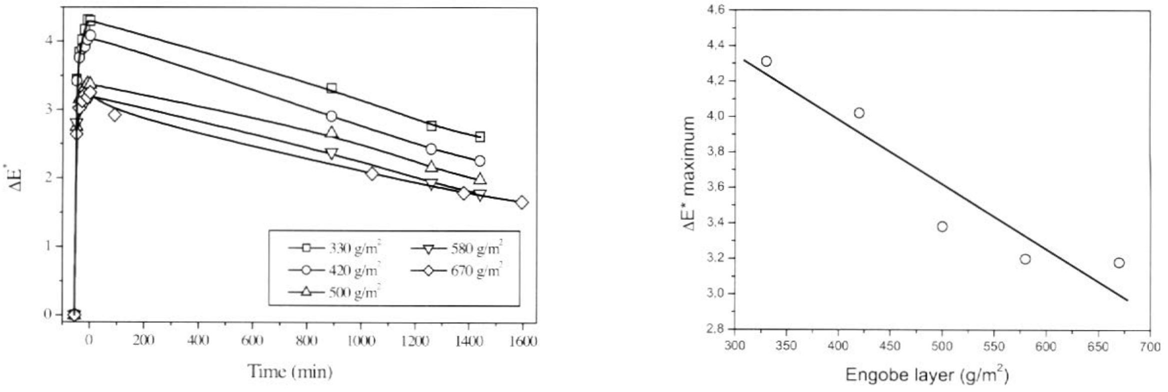


Figure 7. Effect of engobe layer thickness on the water mark in porous tiles.

4.2.2 Engobe composition

Figure 8 plots the results relating to the arising marks using engobe P and F, whose compositions are detailed in Table II. The increase in the meltability provided by replacing the refractory components (clay, kaolin and quartz) by sodium feldspar is observed to affect water mark formation, reducing mark intensity. However, the product made with engobe F still presents a visually noticeable stain, verified by the high ΔE* (2.53) after water immersion.

Table III gives the colorimetric analysis data on the dry tiles, showing that the increase in engobe meltability, besides reducing the water mark also produces a change in colour of the product, evidenced by the variation observed in chromatic co-ordinates L* and b*.

Composition	L*	a*	b*
Engobe P	90.4	0.51	5.18
Engobe F	89.7	0.52	4.00

Table III. Colorimetric analysis of the products made with compositions P and F.

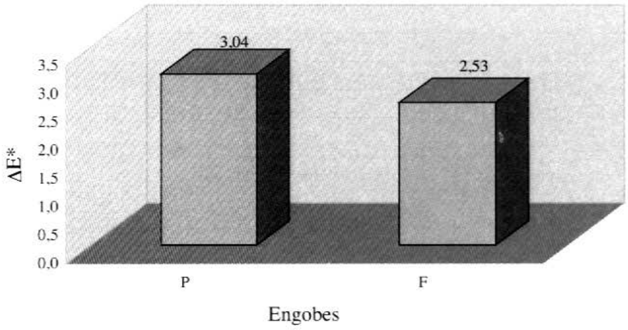


Figure 8. Water mark intensity of engobes P and F.

The effect produced by replacing the clay used in the engobe composition was also evaluated. These tests were conducted using composition F (Table II), which had 12.0% clay. Tests were carried out with four different clays in composition F, subsequently assessing the intensity of the water mark formed in the resulting products (Figure 9) and the arising alterations in colour (Table IV). It can be noted that the nature of the clay used affects colour and engobe staining. Clays can affect the porosity of the engobe layer, both by the packing that they contribute to the composition during the application and because of their meltability in firing. The findings confirm the need to use appropriate clays for engobe development.

In the following tests, the individual effect of the introduction or withdrawal of a given raw material was evaluated, always holding the proportion of other ingredients. First we present the results found on adding and decreasing the zirconium silicate content in composition F. Zirconium silicate was used in two different grain sizes - #325 and #500 - with a view to evaluating the effect of particle size. Holding the proportion of the other raw materials, the #500 zirconium silicate content was varied between 15.0 and 31.0%. For the #325 zirconium silicate the variation was smaller (between 15.0 and 25.0%) in view of the results found (Figure 10 and Table V).

Composition	L*	a*	b*
F – Argentina clay	89.7	0.52	4.00
F –Paraíba clay	90.9	0.54	4.77
F –Suzano clay	91.2	0.32	4.90
F –England clay	86.2	0.24	3.46

Table IV – Effect of the different clays on engobe colour.

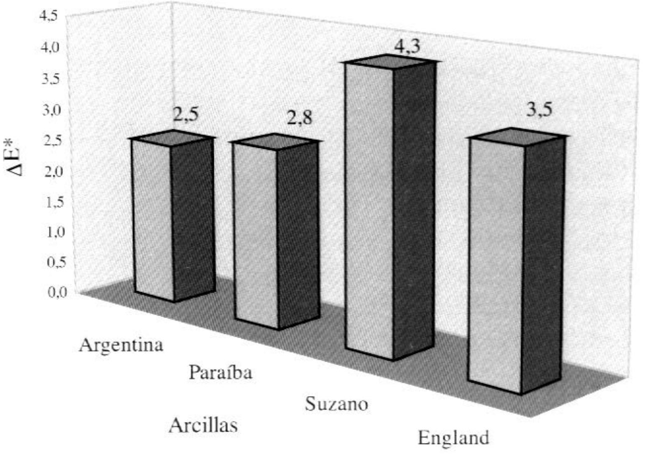


Figure 9- Effect of the different clays on water mark intensity.

Zirconium silicate is a refractory ingredient included in engobe compositions to provide the necessary opacity[7]. Excessive zirconium silicate contents make the engobe unduly refractory, thus raising the tendency to form water marks. The findings indicate the existence of a limit for the use of zirconium silicate, which depends on its initial particle size. In the case of #325 zirconium silicate, adding less than 20.0% to the composition contributed to a reduction in water mark intensity. Above this content, the engobe becomes extremely refractory. The same result applies for #500 zirconium silicate, although in this case the limit for its use is much higher, owing to the finer particles. Of all the zirconium silicate contents tested in the engobe composition, the results obtained with #500 zirconium silicate were better than with #325. This is due to the greater opacifying strength of the smaller particles and lower refractoriness that they contribute to the composition. With regard to the colorimetric analysis of the compositions, it was observed that #500 zirconium silicate was able to provide smaller mark intensity without adversely affecting engobe whiteness. In the case of #325 zirconium silicate, whiteness decreased as a result of the iron impurities contained in the commercial raw material used in the study.

The foregoing results confirm that opacity is not enough to avoid the formation of water marks. It is necessary to have a balance between engobe opacity and meltability, because the pores present in its microstructure can radically reduce opacity when the tiles enter into contact with water.

To study the influence of the fluxing raw materials present in the composition, the contents were varied of the frit, feldspars and raw materials sources of CaO and MgO (talc, diopside and wollastonite).

Figure 11 and Table VI set out the results found with the variation of frit content. All the results refer to the introduction of a zirconium white frit with a high coefficient of expansion and high softening point. It can be observed that adding the frit strikingly raises composition meltability. Good results were achieved with additions of up to 25.0% white frit in the engobe. Above this value, the glazed tile surface began to deteriorate and the excess glassy phase began to reduce engobe opacity. It was also observed that the presence of high frit contents produces decisive alterations in engobe colour, with considerable loss of whiteness.

Composition	L*	a*	b*
Engobe F	89.7	0.52	4.00
F / 15% Zirconium S. #325	89.2	0.47	4.42
F / 18% Zirconium S. #325	89.4	0.37	4.52
F / 21% Zirconium S. #325	87.0	1.52	4.52
F / 23% Zirconium S. #325	87.1	1.37	6.34
F / 25% Zirconium S. #325	86.5	1.44	6.31
F / 15% Zirconium S. #500	89.8	0.29	4.29
F / 18% Zirconium S. #500	89.7	0.52	4.00
F / 21% Zirconium S. #500	90.6	0.28	4.29
F / 23% Zirconium S. #500	91.0	0.27	4.49
F / 25% Zirconium S. #500	90.7	0.26	4.23
F / 28% Zirconium S. #500	91.2	0.03	4.68
F / 31% Zirconium S. #500	89.8	0.25	3.99

Table V. Effect of zirconium silicate particle size and content on engobe colour..

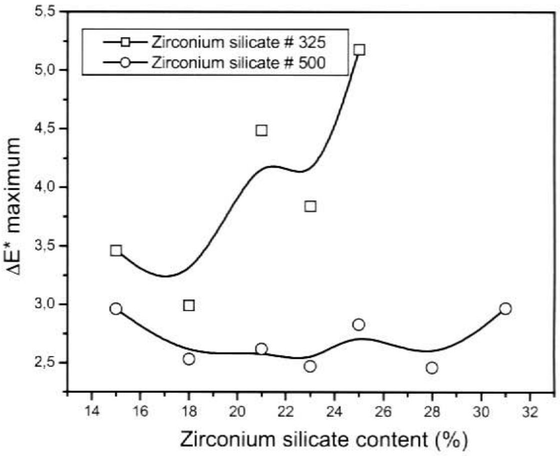


Figure 10. Effect of zirconium silicate particle size and content on the water mark.

Composition	L*	a*	b*
Engobe F	89.7	0.52	4.00
F + 3.0% White frit	88.9	0.35	3.87
F + 5.0% White frit	88.8	0.21	3.72
F + 7.0% White frit	88.3	0.51	3.71
F + 10.0% White frit	88.5	0.13	3.01
F + 13.0% White frit	88.1	0.13	2.59

Table VI. Effect of white frit content on engobe colour.

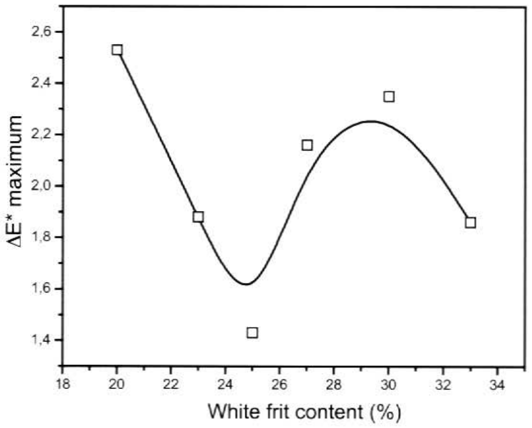


Figure 11. Effect of white frit content on the water mark.

With regard to the results obtained with the increase in alkaline feldspar content in composition F, which already contained 36.6% sodium feldspar (Table II), the results obtained in respect of the objectives of this work were not good. The analysed feldspars (orthoclase, albite and spodumene) did not contribute to reducing staining and produced little alteration of engobe F colour. Spodumene differed slightly from the others by causing a certain drop in engobe whiteness - probably related to the presence of chromophore elements - and a slight reduction in maximum mark intensity on adding high contents to the standard composition (5.0 and 7.0%). Figure 12 and Table VII detail the results found for the studied feldspars.

The raw materials sources of CaO and MgO were studied by virtue of the eutectic compositions that they can form when they are combined with alkaline feldspars. The study involved talc (magnesium silicate), wollastonite (calcium silicate) and diopside (calcium silicate and magnesium), which had low chromophore element contents and contributed CaO and/or MgO. The best results were obtained by introducing talc into composition F. Talc helps form glassy phase, reducing engobe layer porosity. In this sense, it can be considered an important raw material for the development of impervious engobes, although it brings with it some negative effects with regard to the whiteness of the composition. Wollastonite and diopside did not produce the expected result, when they were incorporated into composition F. Figure 13 and Table VIII set out the results.

Composition	L*	a*	b*
Engobe F	89.7	0.52	4.00
F + 3.0% Orthoclase	90.1	0.31	4.17
F + 5.0% Orthoclase	90.3	0.42	4.18
F + 7.0% Orthoclase	90.2	0.30	4.28
F + 3.0% Albite	90.0	0.41	4.01
F + 5.0% Albite	90.3	0.26	3.99
F + 7.0% Albite	90.3	0.35	4.05
F + 3.0% Spodumene	89.0	0.35	4.03
F + 5.0% Spodumene	89.3	0.43	4.10
F + 7.0% Spodumene	89.0	0.51	4.33

Table VII. Effect of alkaline feldspar content on engobe colour.

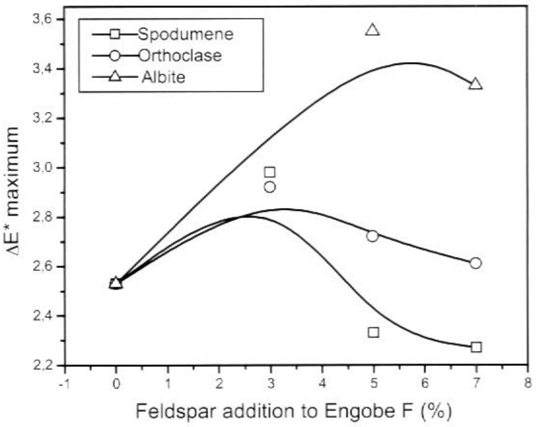


Figure 12. Effect of alkaline feldspar content on the water mark.

Composition	L*	a*	b*
Engobe F	89.7	0.52	4.00
F + 3.0% Talc	88.4	0.40	3.99
F + 5.0% Talc	86.5	0.23	3.28
F + 7.0% Talc	87.1	0.48	3.79
F + 10.0% Talc	88.4	0.06	4.07
F + 13.0% Talc	89.0	0.00	4.57
F + 3.0% Wollastonite	89.3	0.37	3.89
F + 5.0% Wollastonite	89.1	0.28	3.69
F + 7.0% Wollastonite	88.9	0.09	3.61
F + 3.0% Diopside	89.2	0.29	4.12
F + 5.0% Diopside	89.2	0.30	4.18
F + 7.0% Diopside	89.0	0.39	3.78

Table VIII. Effect of talc, wollastonite and diopside content on engobe colour.

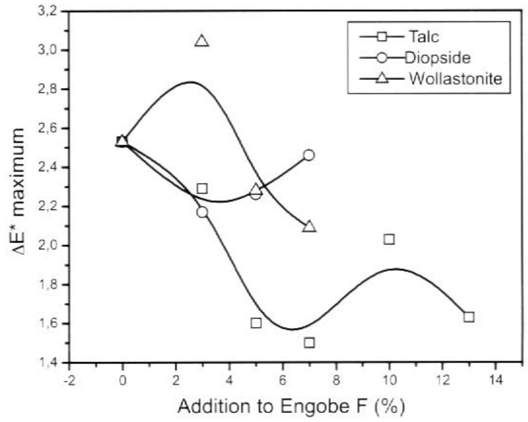


Figure 13. Effect of talc, wollastonite and diopside content on the water mark.

The results indicate that additions of white frit, talc and zirconium silicate contribute to reducing the water mark in porous tile engobes. To conclude the studies on the engobe composition, simultaneous additions were made of frit, talc and zirconium silicate to engobe F, always maintaining the same proportions in the addition of these three raw materials. As the results detailed in Figure 14 and Table IX show, the addition of these three raw materials really contributes to the reduction of the water mark without significantly affecting engobe colour, with contents up to 15.0% (5.0% frit, 5.0% talc and 5.0% #500 zirconium silicate).

After performing numerous tests, some engobe compositions were selected that presented the best results, combining whiteness, relatively low or imperceptible maximum water mark intensity and good glazed surface texture. These engobes presented compatible results with the body and processing conditions used. However, the success of these compositions for other conditions cannot be ensured. The main contribution of the results is in the identification of the effects produced by each raw material, with regard to the reduction or increase of maximum water mark intensity. Nevertheless, an optimum composition should be developed for each specific case, considering the characteristics of the body, glaze and production process. The selected engobe compositions and the results of their characterisation are set out respectively in Tables X and XI.

Composition	L*	a*	b*
Engobe F	89.7	0.52	4.00
F + 7.0% FTZ*	89.8	0.58	4.34
F + 12.0% FTZ*	88.7	0.69	3.69
F + 15.0% FTZ*	88.7	0.57	3.60
F + 21.0% FTZ*	84.7	0.56	3.07

**FTZ = frit +talc + # 500 zirconium silicâte (1:1:1)*

Table IX. Effect of frit, talc and zirconium silicate content on engobe colour.

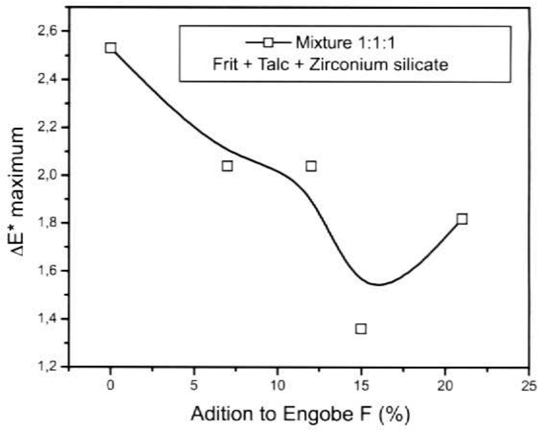


Figure 14. Effect of frit, talc and zirconium silicate content on the water mark.

Raw materials (%)	E1	E2	E3
Argentina clay	10.5	11.2	11.4
Kaolin	2.6	2.8	2.8
Bentonite	0.4	0.4	0.4
Quartz	8.5	9.3	9.6
Sodium feldspar	31.5	34.0	34.8
White frit	22.0	18.8	23.8
Zirconium silicate #500	20.0	17.0	17.2
Talc	4.5	6.5	-
CMC	0.2	0.2	0.2
Tetra-Na pyrophosphate	0.4	0.4	0.4

Table X. Engobe compositions with the best results.

Characteristics	E1	E2	E3
L*	88.7	87.1	88.8
a*	0.57	0.48	0.21
b*	3.60	3.79	3.72
ΔE* max	1.36	1.50	1.43
α_{60-325} ($x10^{-7}$ °C^{-1})	73.6	73.8	74.9

Table XI. Characteristics of the best compositions.

4.2.3 Glaze composition

In certain cases where the composition and the thickness of the engobe layer are not able to keep water marks from arising, there are some alternatives relating to the glaze composition for minimising the problem. In this sense it is necessary to increase glaze layer opacity so that the change in colour of the body is not very noticeable when observed from the glazed tile surface.

Figure 15 and Table XII set out the results found on replacing a transparent glaze by an opaque white glaze. The tests were carried out on the same engobe composition (Engobe F), and it serves to indicate the effect of glaze opacity. The opaque glaze enabled considerably reducing water mark intensity, while the whiteness of the resulting product increased. Thus, opaque glazes can be used successfully to minimise water marks, when this is compatible with the design sought.

Finally, with a view to evaluating the possibilities of reducing water mark intensity in products that use transparent glazes, the possibility was tested of increasing their opacity slightly by incorporating zirconium silicate and opaque white frit in the transparent glaze composition. The results are presented in Table XIII and Figure 16, indicating the effect on product colour and maximum water mark intensity. It was verified that the introduction of fine grain zirconium silicate in the glaze composition is much more effective for constraining the water mark. However, excessive additions can lower glaze meltability unduly and raise its opacity, and can thus impede the application of the decorative elements onto the glaze.

Composition	L*	a*	b*
Transparent Glaze	89.7	0.52	4.00
Opaque White Glaze	91.9	0.13	2.19

Table XII. Effect of the type of glaze on product colour.

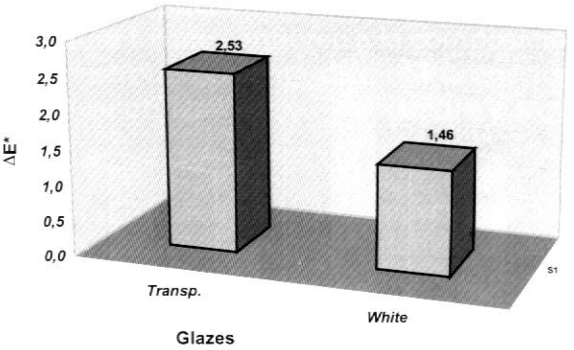


Figure 15. Effect of the type of glaze on water mark intensity.

Composition	L*	a*	b*
Transparent Glaze (ET)	89.7	0.52	4.00
ET + 3.0% White frit	89.4	0.51	4.08
ET + 5.0% White frit	89.9	0.58	4.29
ET + 7.0% White frit	89.8	0.54	4.25
ET + 3.0% Zirconium S. #500	90.4	0.51	4.00
ET + 5.0% Zirconium S. #500	90.5	0.43	3.67
ET + 7.0% Zirconium S. #500	91.0	0.36	3.63

Table XIII. Effect of white frit and zirconium silicate content on engobe colour.

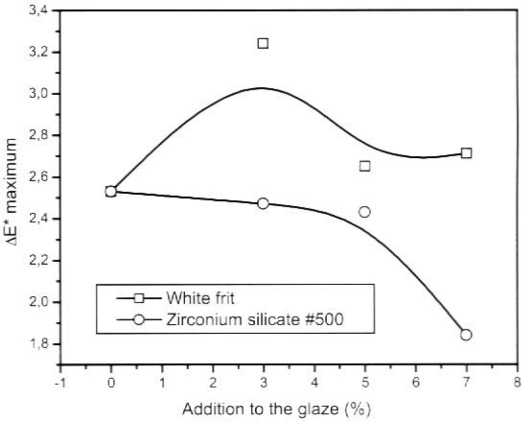


Figure 16. Effect of white frit and zirconium silicate content on the water mark.

5. CONCLUSIONS

The results obtained indicate that the water mark phenomenon arises preferentially in high porosity ceramic tiles, and that the most effective way of minimising this is by adjusting the engobe composition. The use of the colorimetric technique to quantify the water mark allows greater accuracy and sensitivity in the analysis of the results.

To avoid water mark formation it is fundamental for the engobe layer to present high opacity. In this sense, the presence of high zirconium silicate contents, or using thicker engobe layers are measures that were shown to be effective. If the engobe layer is excessively porous, opacity can be adversely affected when the tile absorbs water. For this it is fundamental for the engobe to have high meltability, to provide the smallest possible porosity in the product after firing.

The tests carried out indicate that frit, talc and feldspar contents have a great effect on engobe meltability, while excessive zirconium silicate additions are detrimental to the meltability of the engobe, despite guaranteeing its opacity. The clays should also be selected with due criteria, as they affect engobe layer porosity and hence can increase the possibility of water marks appearing, as well as affecting colour.

Adjustments in the glaze composition can also contribute to minimising the problem. The use of white zirconium glazes or small zirconium silicate additions to transparent glazes also contribute minimising the intensity of the water mark.

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