LIQUID-PHASE SEPARATION IN GLAZES FOR SINGLE-FIRED POROUS WALL TILE

by J. Aparisi(*), M.V. Nuñez(*), A. Moreno(**), Mª J. Orts(**)

(*) Esmalglass, s.a. Villarreal
(**)Instituto de Tecnología Cerámica. Universitat Jaume I. Castellón.
Asociación de Investigación de las Industrias Cerámicas. (AICE). Castellón (España).

ABSTRACT

The appearance of colour differences in fast single-fired porous wall tile with transparent or practically transparent glaze is one of the defects considerably impairing the quality of the finished product.

The separation of immiscible liquid phases during cooling of the glaze in the kiln was shown to be the physico-chemical transformation responsible for changes in colour. The colour of these glazes was shown to be very sensitive to small changes in the composition and limited alterations in the cooling cycle of the ware in the kiln. A method is proposed, based on the measurements of the chromatic coordinates of the glaze obtained by subjecting it to different thermal treatment, for determining the sensitivity of the glaze to changes in colour by alterations in the cooling cycle.

1. INTRODUCTION

The appearance of colour differences in fast single-fired porous wall tile with virtually transparent glaze is one of the defects considerably impairing the quality of the finished product.

The colour of these glazes has been shown industrially to be extremely sensitive to small changes in the composition and in the cooling cycle. The latter seems to indicate that a series of physico-chemical transformations (immiscible liquid-phase separation, crystallization of new phases) takes place during cooling of the ware in the kiln, which appear macroscopically as a change in colour of the glaze.

This kind of glaze is characterized by bearing a high percentage of alkaline earth oxides and zinc oxide as well as a considerable amount of boron oxide. These materials may therefore be expected to show a great tendency to separate into immiscible liquids or even to devitrify crystalline phases, as may be observed from the corresponding immiscibilty diagrams (1) (2) (Figure 1). There is in fact a broad immiscibility domain for these systems where many of the compositions used as glazes for single-fired tiles are to be found.

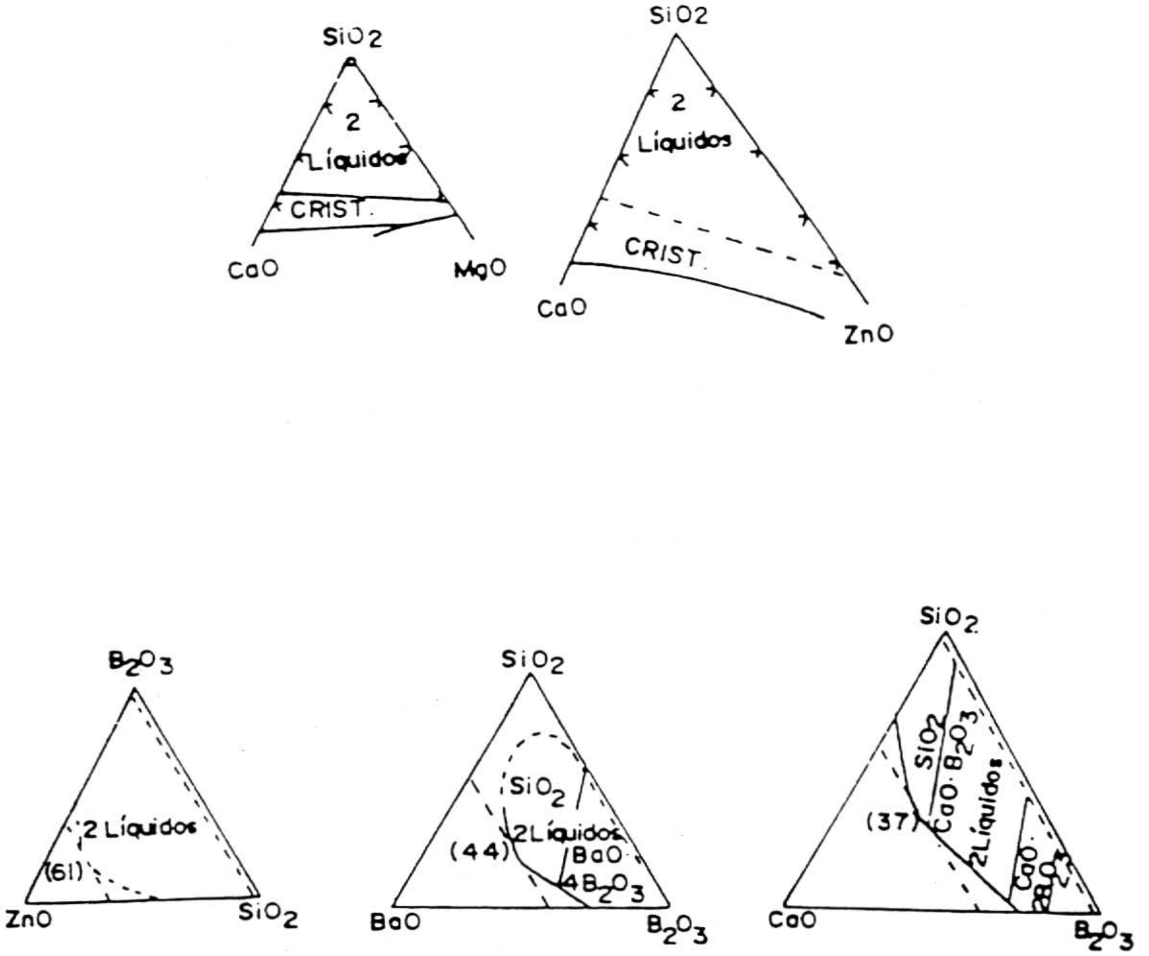

Figure 1. Immiscibility diagrams of some ternary systems.

2. AIMS

In this study the causes of changes in colour of the glaze are analyzed with a view to acquiring enough information to formulate new compositions which avoid or minimize this defect.

A series of experiments was therefore programmed to achieve the following aims:

i) To determine the nature of the physico-chemical transformations responsible for the change in colour of the glaze on cooling in order to eliminate or minimize this defect.

ii) To determine the temperature interval in which these changes in colour take place at the greatest rate in order to choose a suitable cooling cycle and establish the influence of this firing stage on this phenomenon.

3. MATERIALS AND EXPERIMENTAL PROCEDURE

3.1 Materials

In order to carry out this study, a group of frits used in obtaining transparent glazes over porous bodies by fast single firing were utilized. Their chemical compositions are detailed in Figure 2. Although differences in composition among the different frits are to be observed, they all bear a great amount of CaO and ZnO, as well as BaO in some instances.

The sealing, transformation, and softening temperature values of these frits are detailed in Figures 3, 4 and 5. All present the typical values for frits used in single-fired porous wall tile manufacture.

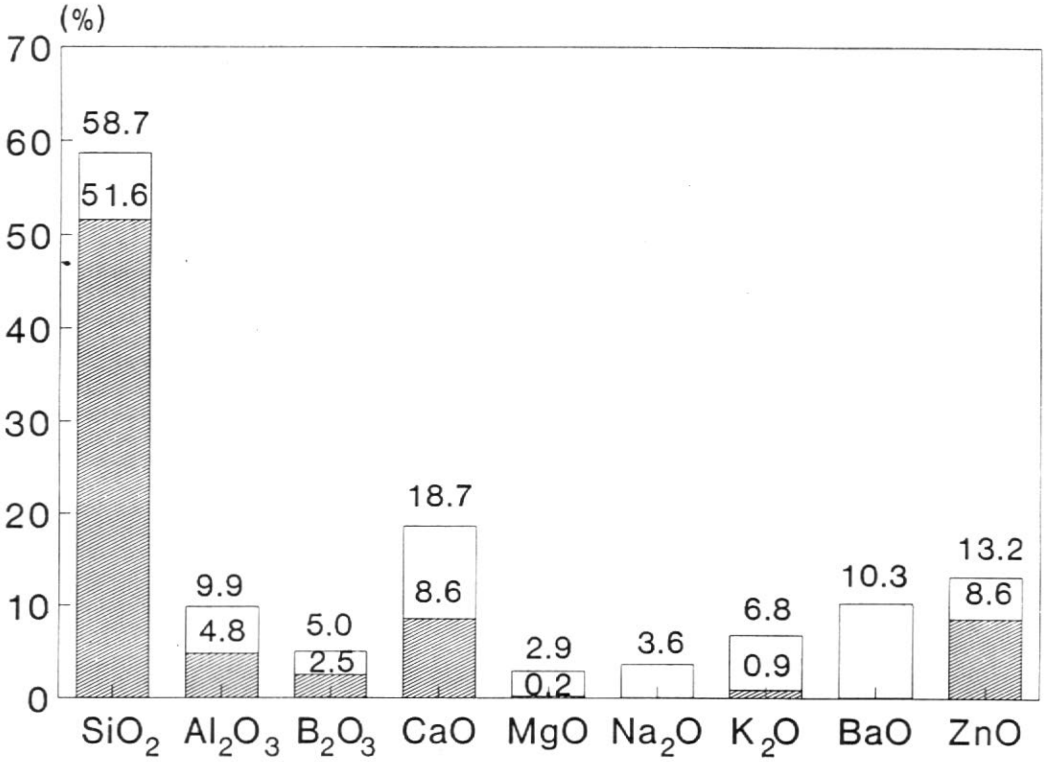

Figure 2. Interval of compositions studied.

3.2 Experimental

3.2.1 Sample preparation

Glaze suspensions were prepared by grinding each frit in a laboratory ball mill with 5% kaolin and 0.3% C.M.C. Operating conditions were as follows: Suspension density 1.65 g/cm³. and 2% grind oversize fraction at 40 µm. The glaze suspension was sprayed onto a single-fired porous redware body which had previously been fired at 1100°C, while the amount of glaze applied, 0.7 g/cm, was held as constant as possible.

3.2.2 Thermal treatment.

3.2.2.1 Non-isothermal experiments.

A series of experiments was run with each of the frits, keeping the firing cycle constant and modifying the kind of cooling in order to compare the changes in colouring the glazes undergo during the cooling stage of the firing operation and to determine the temperature interval in which this phenomenon takes place at the greatest rate. The thermal cycles used are shown in Figure 6. As may be observed in this figure, each test specimen was fired up to 1100°C and cooled in the kiln according to a slow (A) or a fast (B) cycle until reaching a certain temperature. The test specimen was then taken out of the kiln and left to cool in ambient conditions. The arrows in the figure indicate the temperature at which removal from the kiln took place.

The thickness of the glaze layer and its chromatic coordinates (Section 3.2.3) were determined in the cold test pieces. The test pieces with a markedly different thickness in their glaze layer from the preset value were rejected.

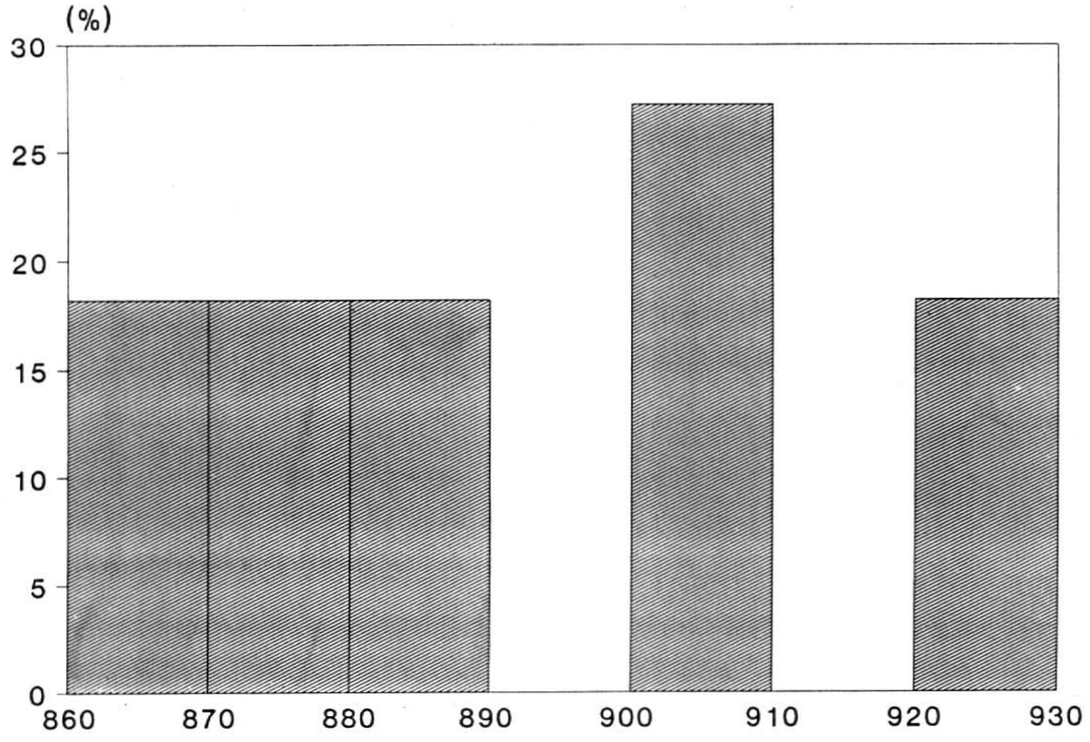

Figure 3. Sealing temperatures of the frits used.

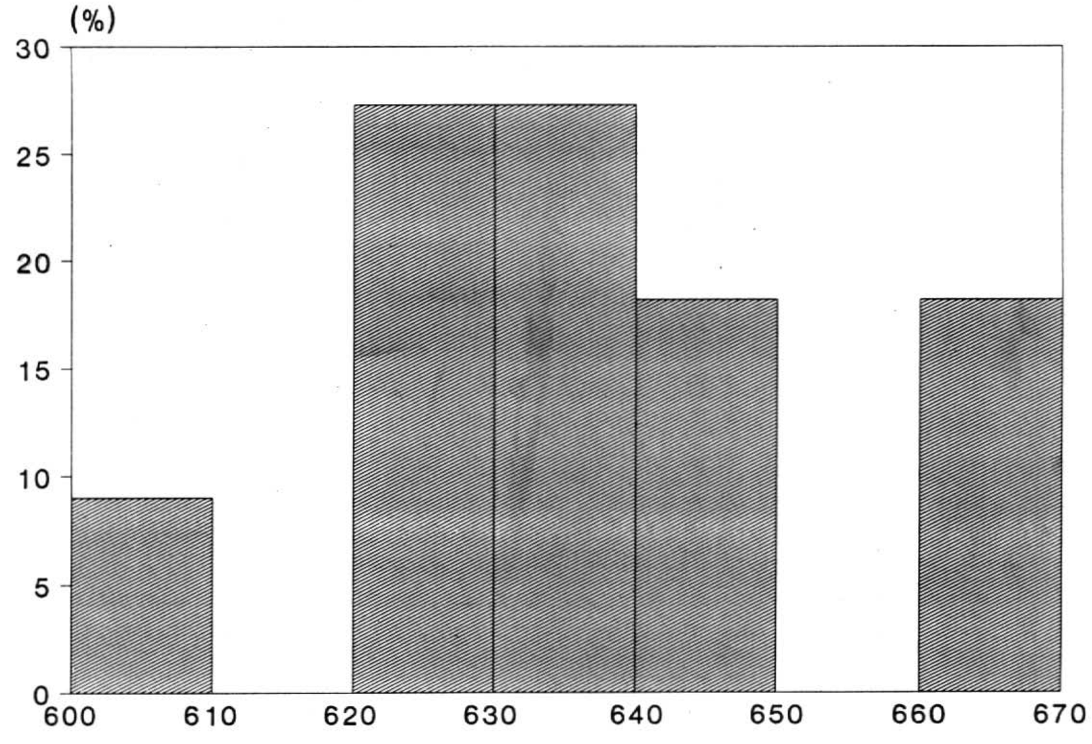

Figure 4. Transformation temperatures of the frits used.

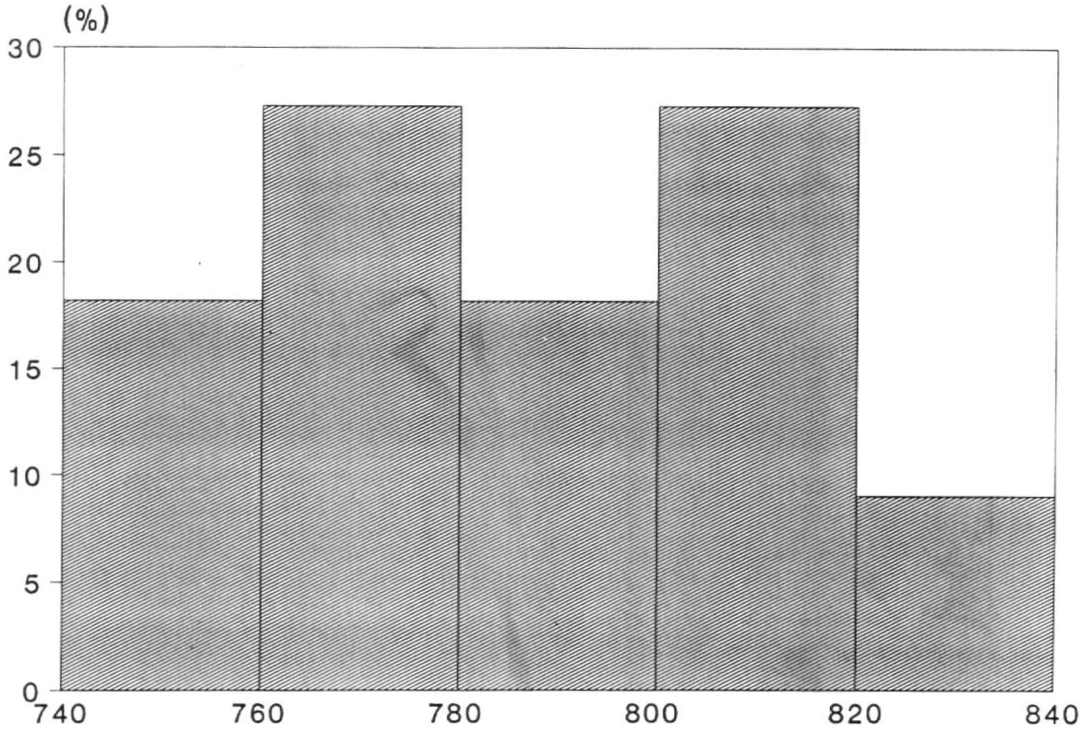

Figure 5. Softening temperatures of the frits used.

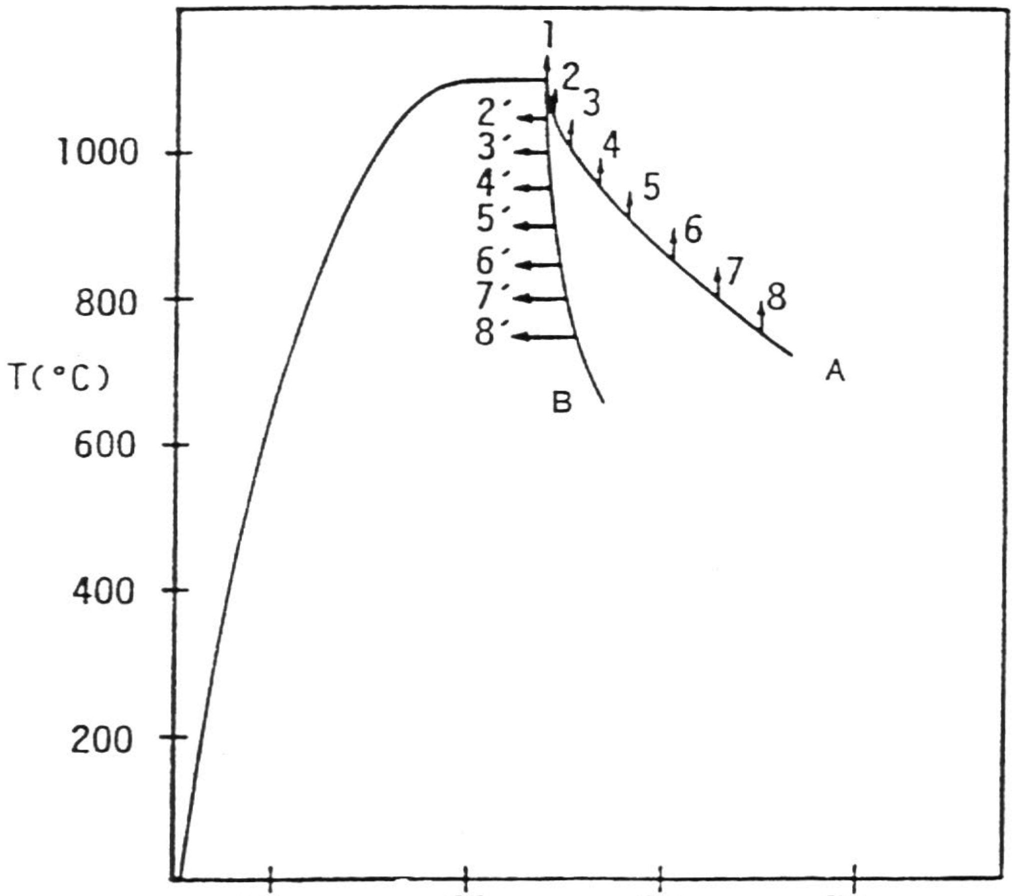

Figure 6. Non-isothermal thermal treatment used. (The arrows indicate temperature and time at which test pieces were removed from the kiln).

3.2.2.2 Isothermal experiments

A series of isothermal experiments was conducted to determine the influence of temperature on the rate at which changes in colour take place in the glaze.

The thermal treatment carried out is schematized in Figure 7. It involved subjecting the fired test pieces taken from the kiln at 1100°C to differing thermal treatment.

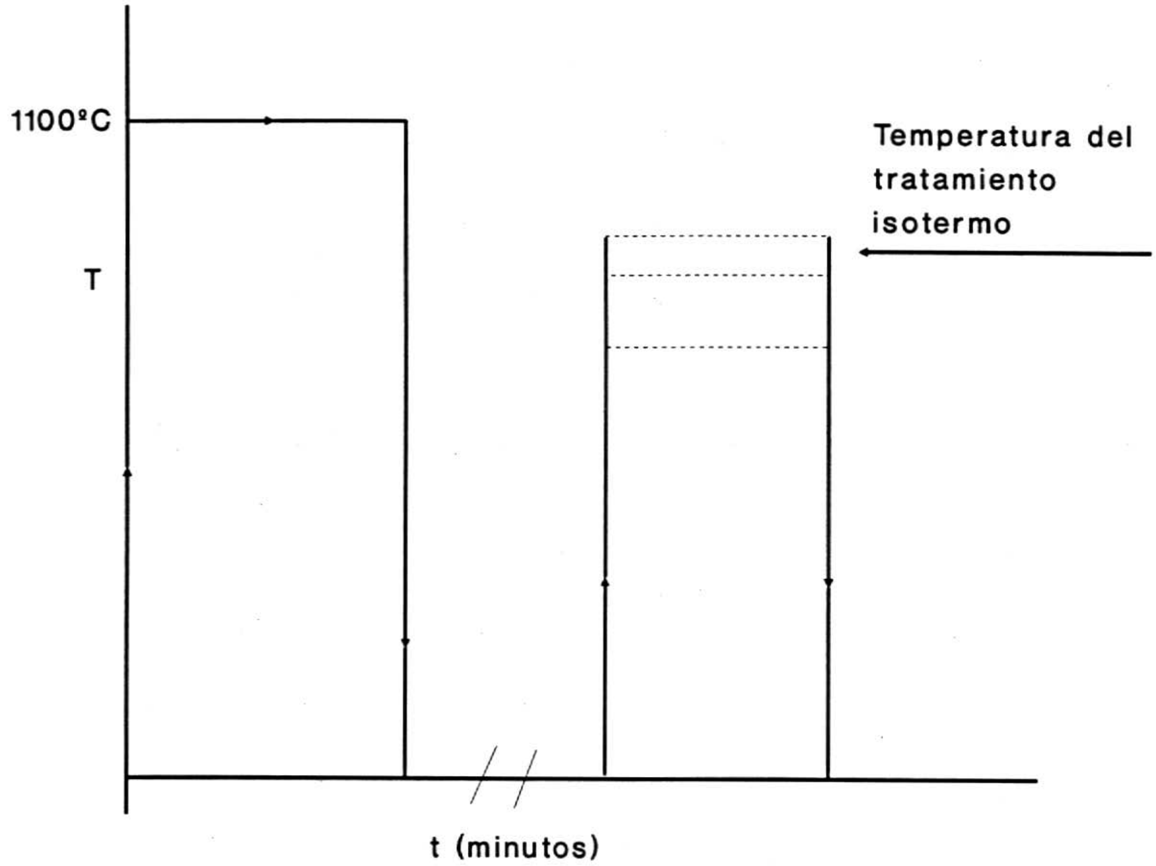

Figure 7. Isothermal treatment method to determine the rate of change in colour of the glazes.

3.2.3 Determination of the change in colour in the glazes.

The changes in colour in each glaze, which take place on cooling of the ware, were quantified as the difference between the values of the chromatic coordinates of the glaze applied on the test piece removed from the kiln at 1100°C and the values corresponding to those involved in the remaining thermal treatment. As pointed out above (Section 3.2.1), glaze was applied on bodies previously fired at 1100°C so that any possible change in colour of the body would not affect the results.

3.2.3.1 Determination of the chromatic coordinates of the glazed piece.

These were determined by means of a tristimulus colorimeter, model LFM-3, supplied by the firm Dr. Lange. The CIE 1976 (CIELAB) measuring system was used. This is based on colour description by using three rectangular coordinates (L*, a* and b*). The relation between these parameters and colour are schematized in Figure 8. In order to reduce experimental error, five measurements were run on each test specimen and the mean value was computed.

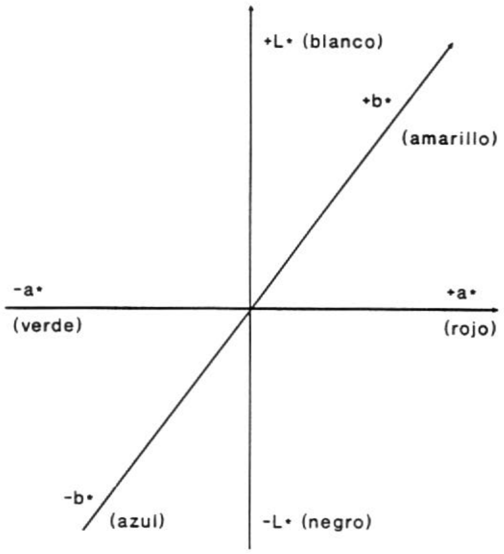

Figure 8. CIELAB system of chromatic coordinates. (green; light green; light yellow; yellow red; dirty red; blue black; blue)

3.2.3.2 Calculation of colour differences.

The standard ASTM D-2244-85 method () was used.

According to this method, colour difference $(\Delta C)^*$ between a certain colour (C^*) described by its chromatic coordinates (L^*, a^* and b^*) and the reference colour (C_o^*) with coordinates (L_o^*, a_o^* and b_o^*) is given by the equation:

$$\Delta C^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where:

$$\Delta L^* = L^* - Lo^*$$
$$\Delta a^* = a^* - ao^*$$
$$\Delta b^* = b^* - bo^*$$

A glazed piece fired at 1100°C and removed from the kiln at this temperature was taken as reference colour (Co^*). The values for ΔL^*, Δa^* and Δb^* therefore indicate the difference between the values of the chromatic components white, red and blue of a glazed piece and those of the reference piece.

4. RESULTS AND DISCUSSION

4.1 Changes in colour undergone by the glazes according to the cooling cycle they were subjected to.

In Figures 9 and 10 the bounding colour difference values found for a glaze fired at 1100°C and removed from the kiln at this temperature and the findings obtained on letting it cool inside the kiln to ambient temperature are shown for the glazes studied, according to each of the two above-mentioned cycles (Figure 6).

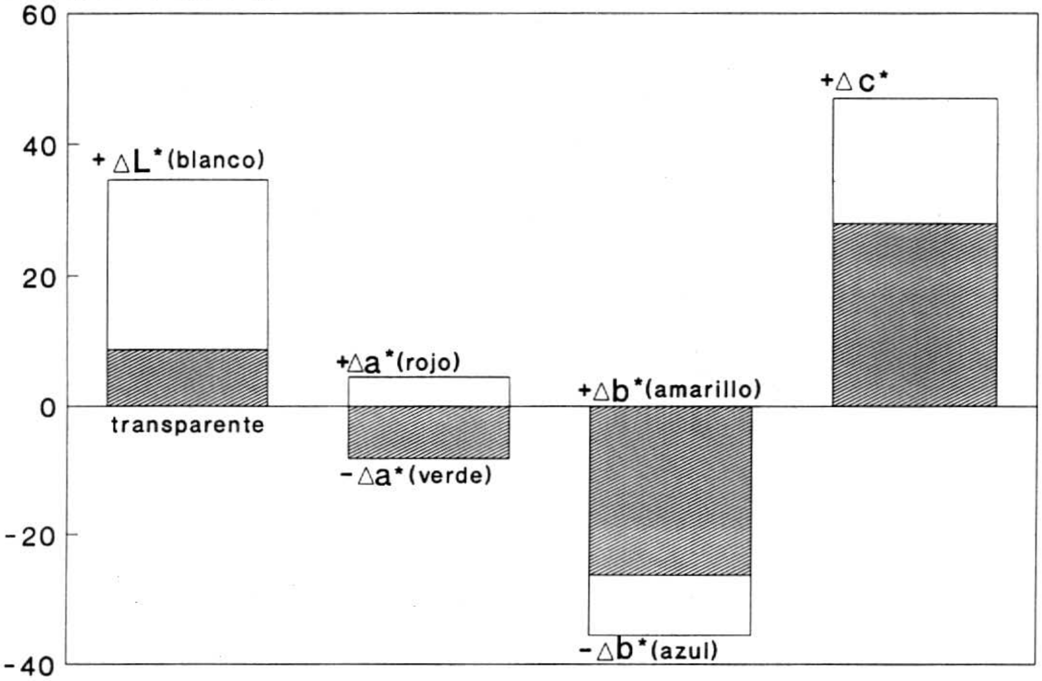

Figure 9. Colour difference (ΔC*) and chromatic coordinates (ΔL*, Δb* and Δa*) between the glaze fired and removed from the kiln at 1100°C (virtually transparent) and the glazes after cooling by a slow cycle (type A). Cooling time from 1100 to 750°C was 25 min.

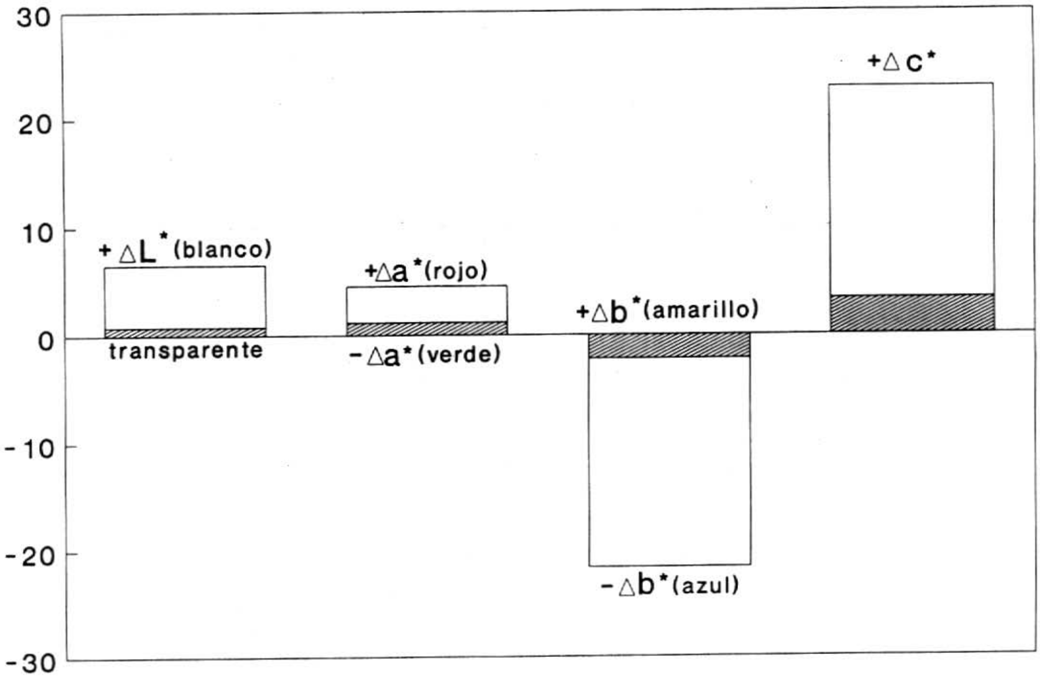

Figure 10. Colour difference (ΔC*) and chromatic coordinates (ΔL*, Δb* and Δa*) between the glaze fired and removed from the kiln at 1100°C (virtually transparent) and the glazes after cooling by a fast cycle (type B). Cooling time from 1100 to 750°C was 3.5 min.

The following may be concluded on analysis of these figures:

- The magnitude of the change in colour the glaze undergoes on cooling decreases considerably when the cooling rate of the ware increases.
- All the studied glazes showed changes in colour to a greater or lesser extent on cooling. However, some performed better and even managed not to show any appreciable changes in colour when cooled at high rates.
- In each case the change in colour was due to an increase in the blue (-Δb*) and white (ΔL*) chromatic component.

The change in colour one of the studied frits underwent when this glaze was cooled according to cycle A, is plotted in Figure 11.

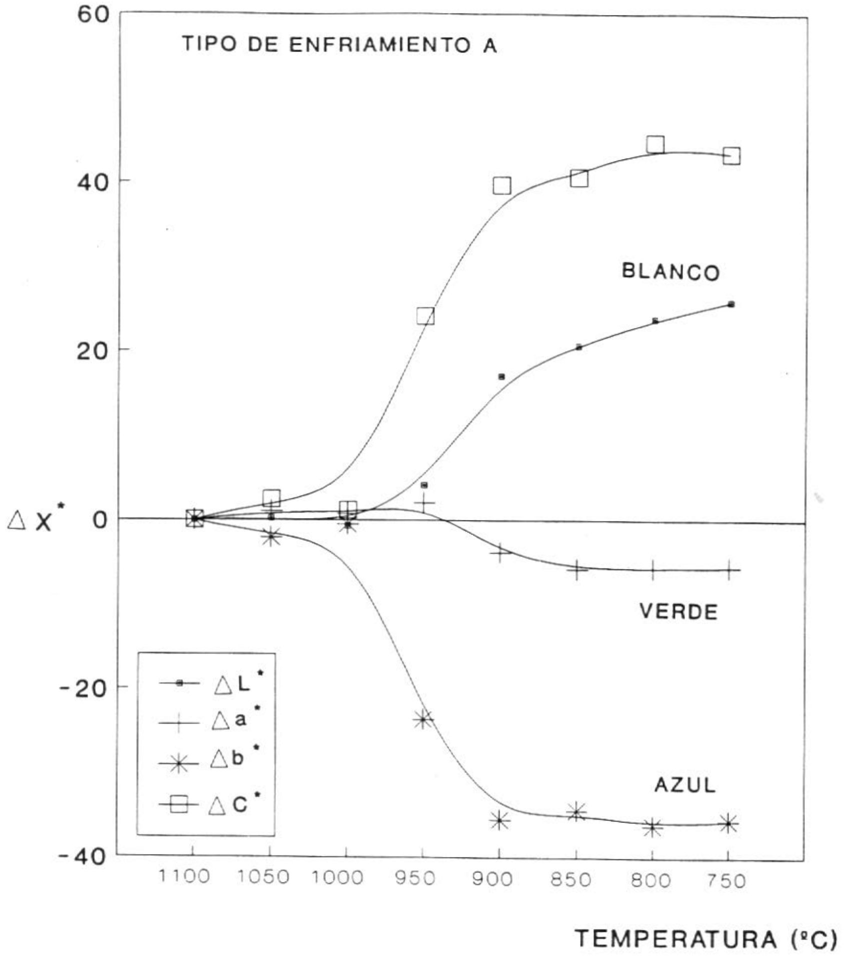

Figure 11. Variation of the differences between the values of the chromatic components of the glaze and those corresponding to the reference piece with cooling time.

In this glaze the change in colour is observed to take place in a temperature interval between 1000 and 900 °C. Analogous findings were obtained for the other glazes studied, although the temperature interval in which the change in colour takes place at the greatest rate and the magnitude of the transformation are different.

The above seems to indicate that the change in colour of the glaze on cooling is due to immiscible liquid-phase separation and/or devitrification of crystalline phases. In fact, the maximum rate of change in colour takes place at a temperature interval in which the glaze is fluid enough to allow the above-mentioned transformations to take place. On the contrary, at low temperatures viscosity of the glaze is so great that such transformations do not take place at an appreciable rate. At high temperatures, close to peak temperature, the thermodynamic tendency to nucleate is so slight that although viscosity of the glaze is also low, no nuclei can form. (3) (4)

4.2 Kinetics of changes in colour of the glaze.

A series of isothermal experiments was conducted with one of the frits which showed a great tendency to change in colour on cooling, according to the procedure described in Section 3.2.2.2.

In Figure 12 the differences are plotted between the values of the chromatic coordinates of the glazed pieces treated at different temperatures and dwell times and those of the reference piece (taken from the kiln at 1100°C), in order to determine the temperature interval in which changes in colour take place at the greatest rate.

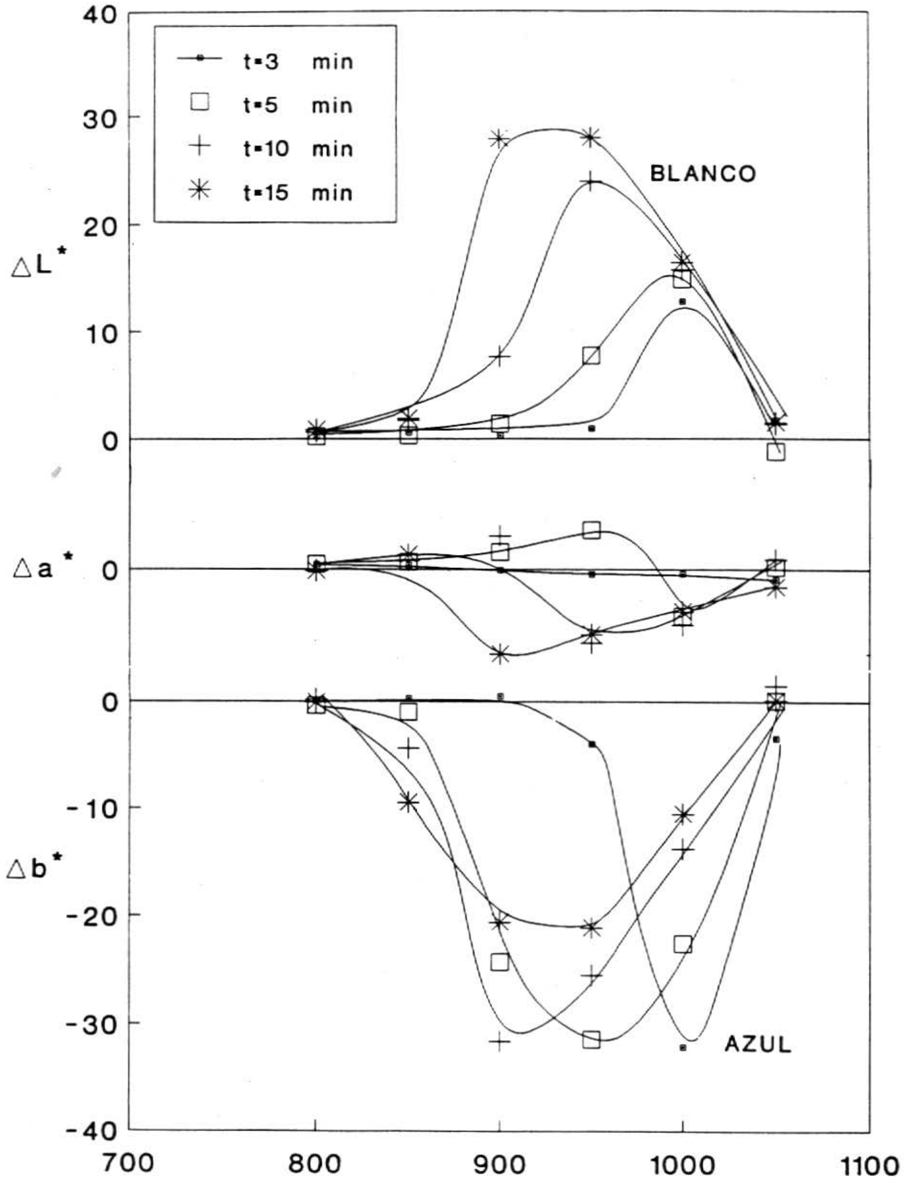

Figure 12. Evolution of the chromatic components of the glaze with isothermal temperature treatment, for different dwell times.

In Figure 13, the evolution of the chromatic coordinates blue and white are plotted with dwell times for the temperatures at which changes in colour develop at the greatest rate, in order to determine the effect of temperature on the rate of change in colour of the glaze.

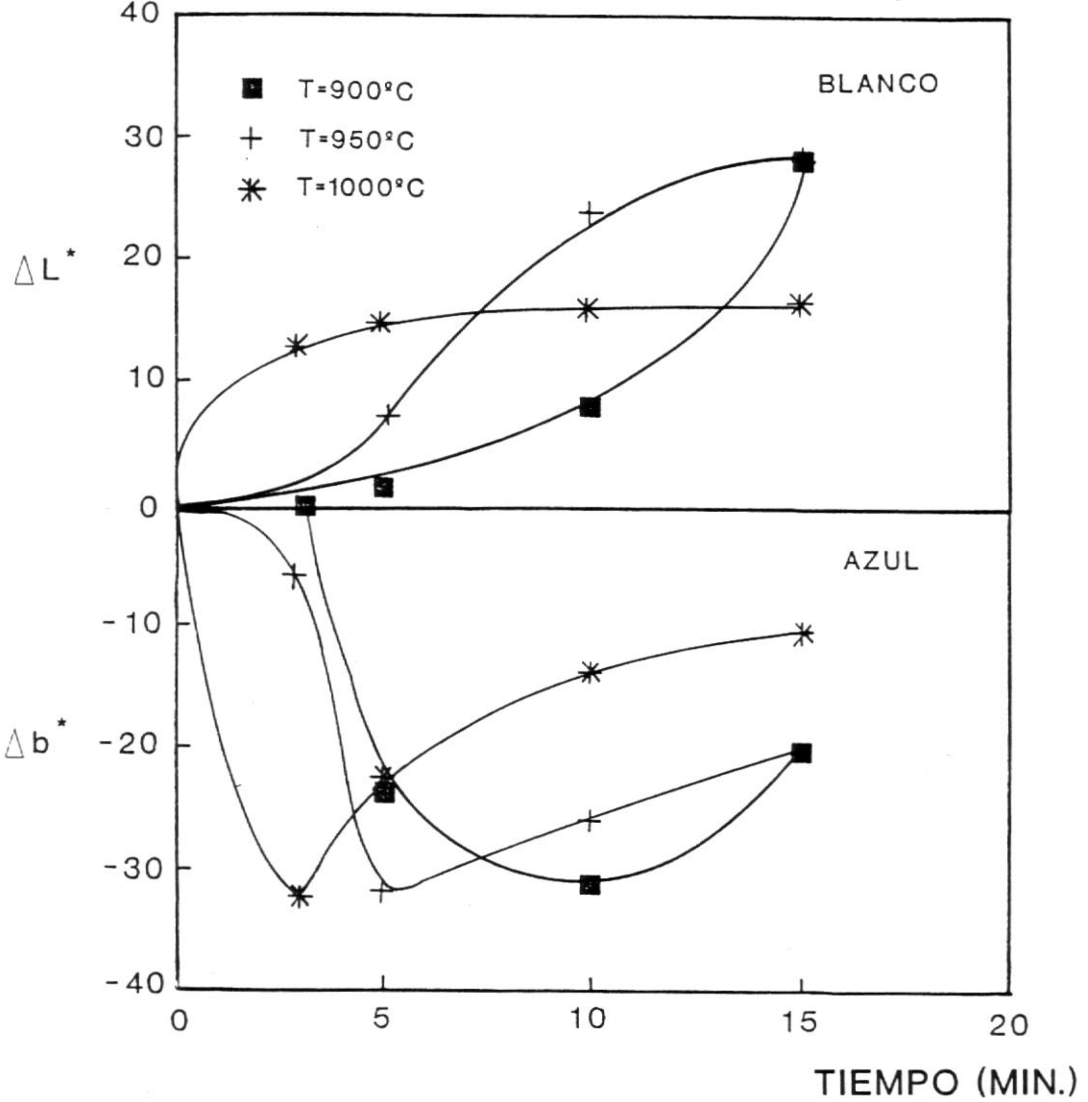

Figure 13. Variation of the chromatic coordinates of the glaze with dwell times at different temperatures.

On analyzing these plots, the following conclusions may be drawn:

(i) The temperature interval in which colour changes take place in the glaze at an appreciable rate lies between 800 and 1050°C (Figure 12).

(ii) The temperature at which the colour difference of the piece is the greatest (for both blue and white), increases as dwell time decreases (Figure 12).

(iii) The white chromatic component (ΔL*) increases as dwell time of the glaze increases for all the temperatures tested (Figure 13). On the contrary, the blue chromatic component reaches its maximum value after a certain time and then drops. In fact for this glaze, at temperatures close to 900°C, maximum blueness is reached after a ten-minute dwell time. Blueness decreases progressively and whiteness increases on incrementing dwell time at this temperature (Figure 13).

(iv) On comparing the evolution of the chromatic components with dwell time at a certain temperature (Figure 13), the change in colors of the glazes is observed to follow the sequence:

Transparent - blue - bluish white - white, in each case.

The fact that in both isothermal as well as non-isothermal treatment (Section 4.1), blueness appears as the first observed change in colour of the glaze, to then turn white, indicates that the physico-chemical transformation responsible for this phenomenon is immiscible liquid-phase separation. In fact, blueness is due to mainly the shortest wavelength radiation of the visible spectrum being absorbed by the glaze. This absorption is characteristic for glazes bearing nucleated phase separation in which the size of the drops dispersed in the matrix is limited. On increasing the duration of thermal treatment, drop size grows and/or they coalesce, which entails absorption of radiation with a longer wavelength and the glaze therefore appears white and opaque (6).

4.3 Nature of the physico-chemical transformations responsible for changes in colour of the glaze on cooling.

In the foregoing section, immiscible liquid-phase separation was suggested as being the likely cause of changes in colour of the glaze on cooling. In order to confirm this assumption some isothermally treated test pieces were chosen for observation by scanning electron microscopy (SEM).

Transparent glazes were shown to contain nucleated separation of immiscible liquid phases with a very small drop size (<0.2μm) (Figure 14).

Furthermore, bluish transparent glazes (Figure 15 and 16) were also observed to bear nucleated phase separation. However, drop size was greater (0.2μm) so that on mainly absorbing shorter visible wavelength radiation they turned bluish.

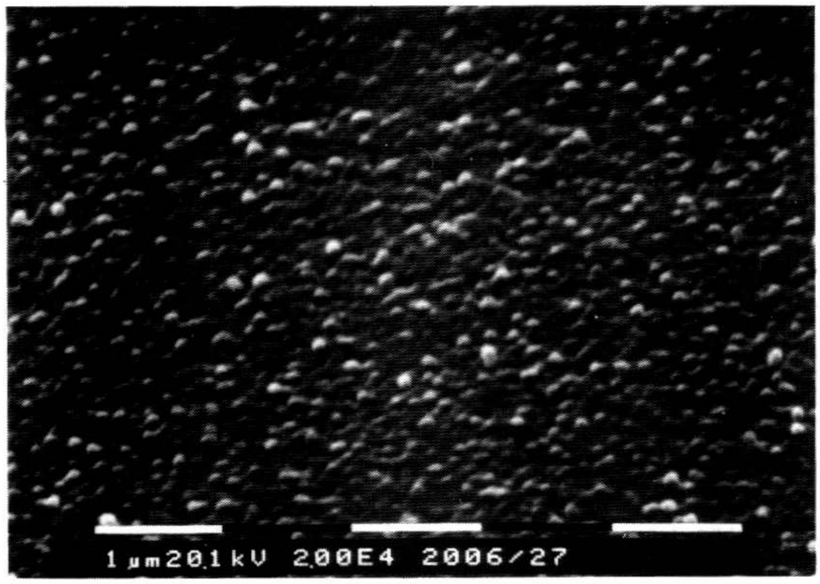

Figure 14. Microstructure of a transparent glaze.

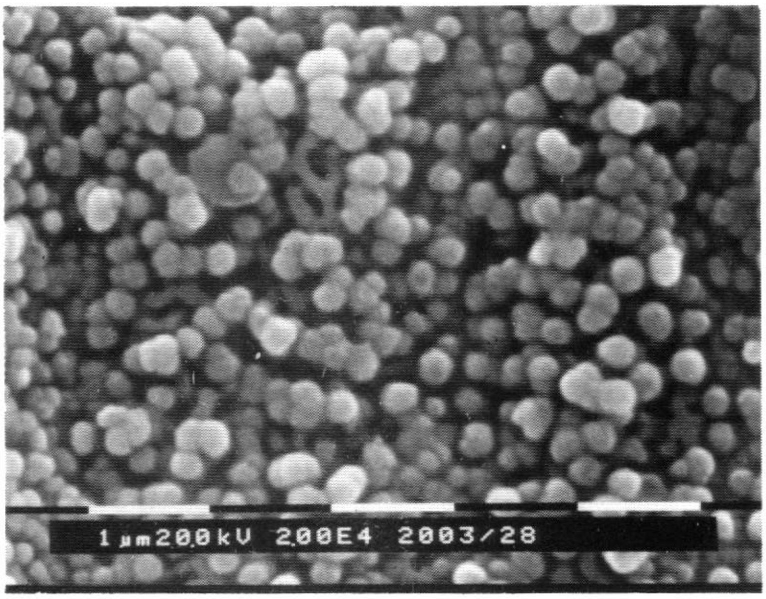

Figure 15. Microstructure of a bluish glaze.

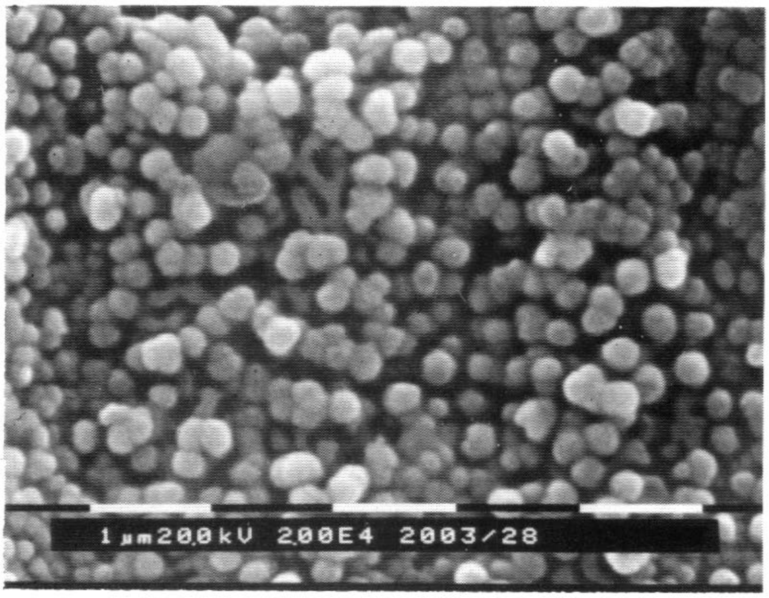

Figure 16. Microstructure of a bluish glaze.

White (opaque) glazes were similarly observed to bear drops of immiscible liquid phase which had coalesced (Figures 17 and 18). The increase in size of the dispersed phase involves overall absorption in the visible light spectrum thus giving the glaze a white appearance.

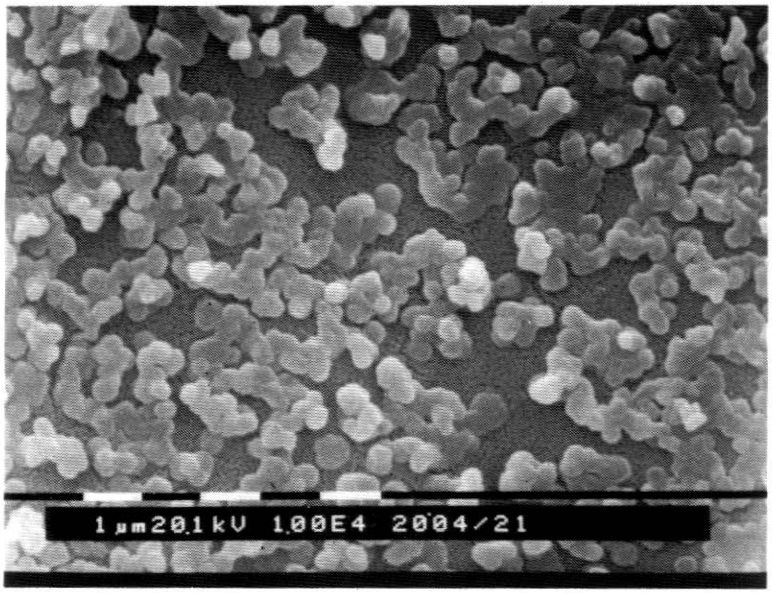

Figure 17. Microstructure of a bluish-white glaze.

Figure 18. Microstructure of a white glaze.

It may be concluded from the foregoing that the colour of the glaze will depend upon the number of dispersed drops and their size. Therefore, as nucleation of small drops and their growth and/or coalescence take place at a great rate and at partially overlapping temperature intervals in this glaze, holding the colour of the glaze or periodically obtaining transparent slightly bluish glazes would be extremely complicated (Figure 19).

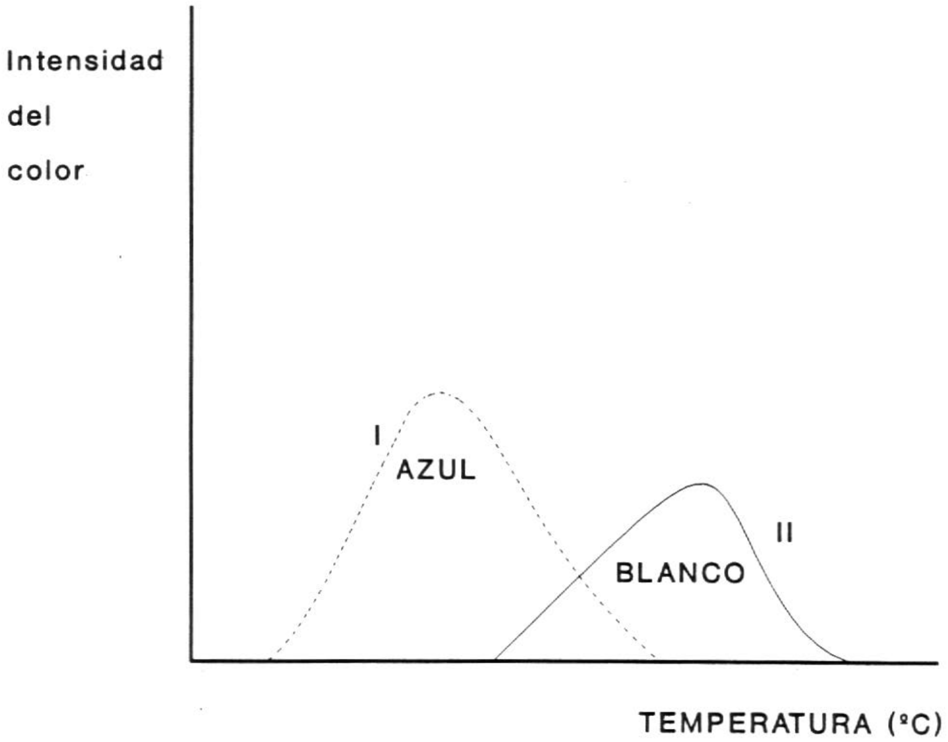

Figure 19. Nucleation (I) and growth (II) curves.

4.4 Isochromatic curves.

These curves were experimentally obtained by means of isothermal techniques (Section 3.2.2.2) and plot the pairs of values, temperature and dwell time at that temperature, where the glaze reaches the same blueness (Figure 20) or whiteness index values (Figure 21). The following information may easily be acquired by using this kind of plot:

(i) The sensitivity of a glaze to change in colour on cooling. In fact, the shorter the time in which a certain change of colour takes place the more difficult it becomes for the glaze to keep its original colour on cooling.

(ii) The temperature at which the change in colour of the glaze develops at the greatest rate. That is, the temperature at which the glaze undergoes a certain change in colour with the shortest dwell time.

(iii) Establishing the temperature and time intervals in which there is no change in glaze colour.

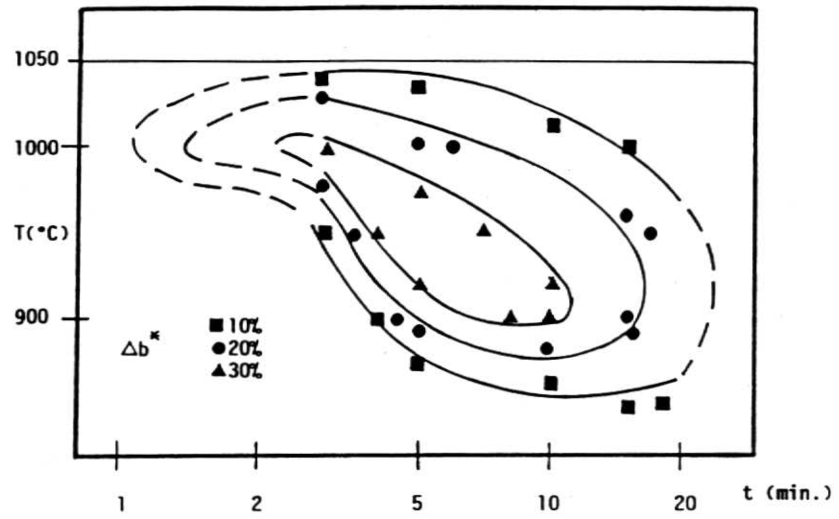

Figure 20. Curves of the same blueness index values (Δb*) obtained from isothermal treatment.

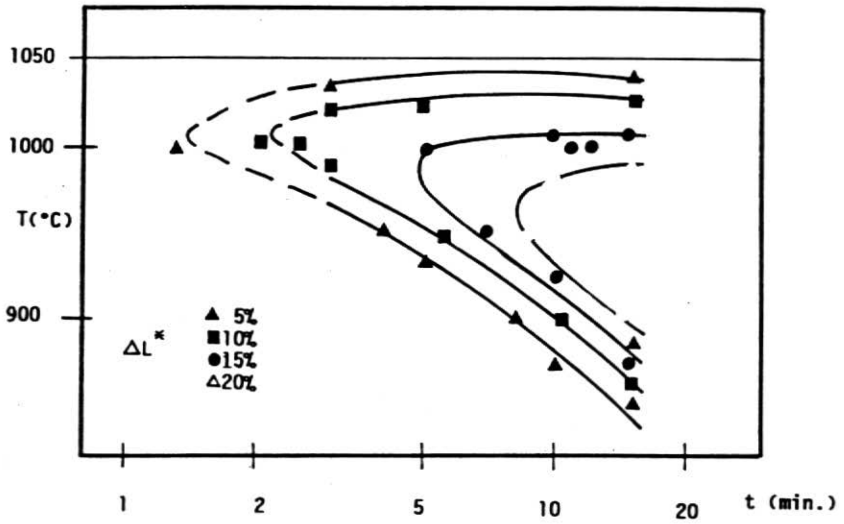

Figure 21. Curves of the same whiteness index values (ΔL*) obtained from isothermal treatment.

On analyzing Figures 20 and 21 the following conclusions may be drawn:

(i) For this frit, the greatest rate at which change in colour takes place lies at a temperature of about 1000°C. At this temperature a dwell time of 1 to 2 minutes leads to a considerable increase in blueness and opacity (whiteness) of the frit. At lower or higher temperatures than the above the time required to produce appreciable change in colour is longer. For temperatures above 1050°C or below 850°C the rate at which changes in colour develop is very low.

(ii) The temperature and time intervals in which this glaze shows a certain blueness and whiteness are extremely narrow, thus rendering it extremely complicated to hold the colour.

(iii) On superimposing Figures 20 and 21, the areas in which the glaze turns blue virtually coincide with those in which the glaze shows opalescence. These findings confirm the extreme difficulty of obtaining transparent blue glazes which are not opalescent with this frit.

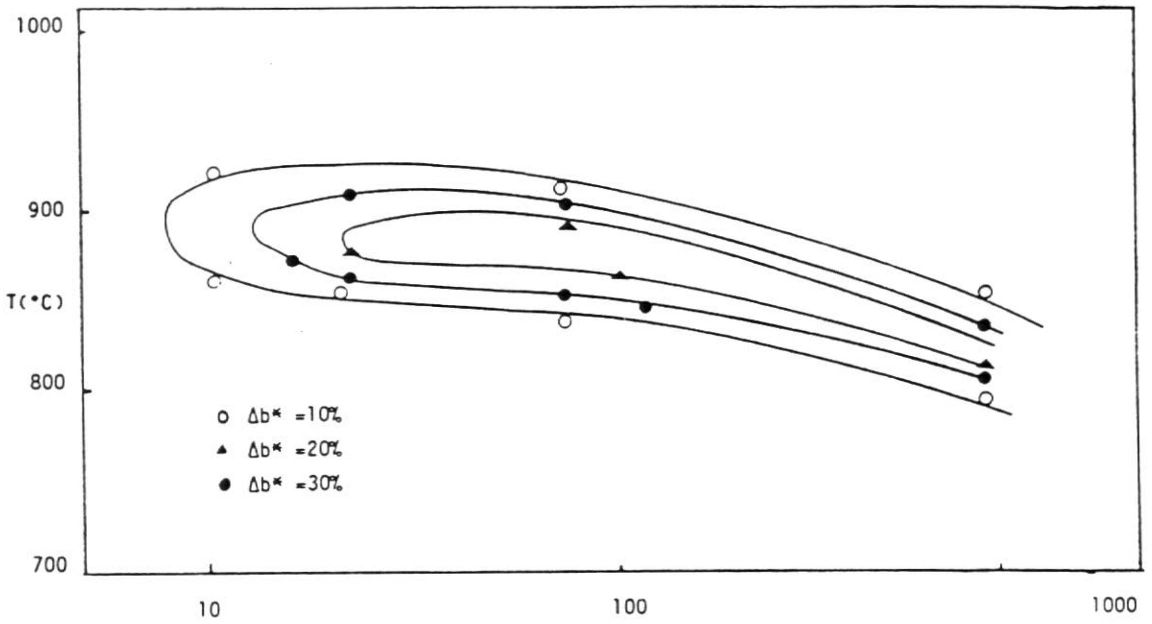

Figure 22. Curves of the same blueness index values (Δb*) for a glaze with little tendency to liquid-phase separation.

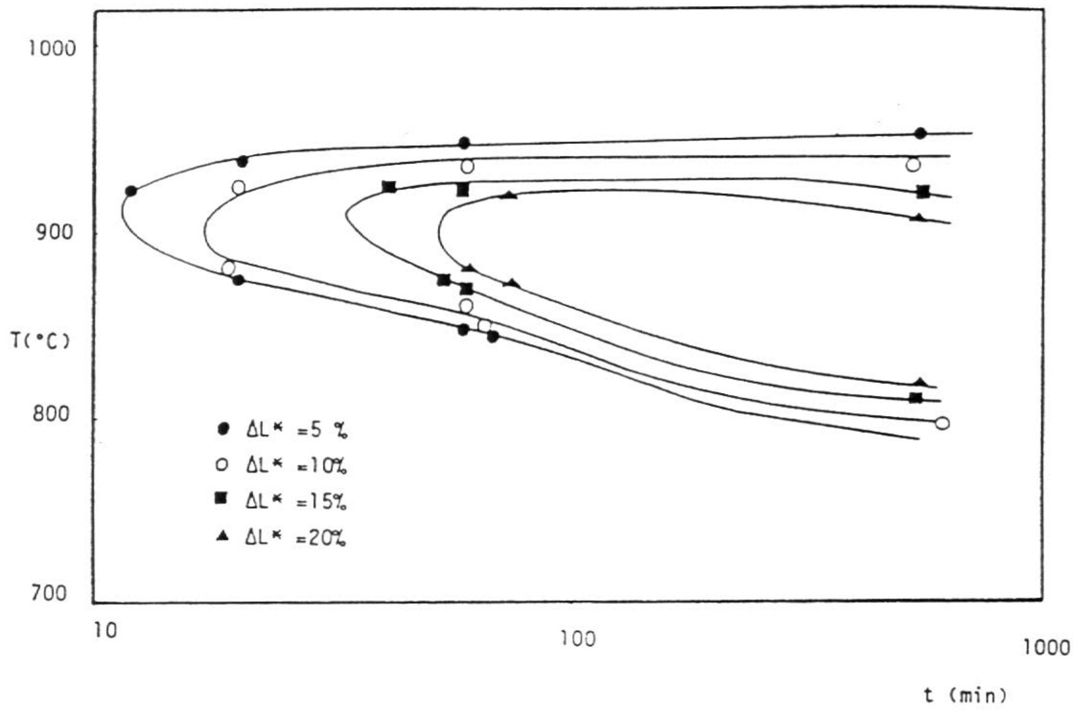

Figure 23. Curves of the same whiteness index values (ΔL*) obtained from isothermal treatment.

It has been possible to obtain frits for single-fired porous tile with little tendency to change in colour on cooling, on the basis of the influence exerted by the frit composition on liquid-phase separation as well as by using the techniques described above.

The isochromatic diagrams corresponding to one of these frits are plotted in Figures 22 and 23.

It has likewise been observed that slight variations in frit composition considerably influence the tendency for changes in colour to develop on cooling of the glaze. This all entails the need to dispose of a very strict monitoring system both for the raw materials as well as the frit elaboration process to obtain good transparent glazes.

5. CONCLUSIONS

The following conclusions may be drawn from the findings obtained in this study:

(i) Immiscible liquid-phase separation was shown to be the physico-chemical transformation responsible for changes in colour of the glaze on cooling in the kiln, for this kind of glaze. However, the magnitude of this phenomenon largely depends on frit composition and the cooling rate used on firing.

(ii) On studying the evolution of the chromatic coordinates of the glazes subjected to different thermal treatment, change in colour was in each case shown to follow the sequence: transparent -blue - bluish white - white. The study of the microstructures of these glazes showed these changes in colour to be associated with growth and/or coalescence of immiscible phases separated by nucleation.

(iii) The isochromatic diagrams described above, which provide data concerning the sensitivity of the glaze to changes in colour and the temperature at which the transformation takes place at the greatest rate, allow frit compositions and the most suitable cooling cycles to be chosen to avoid these changes in colour of the glaze. It is possible to obtain good transparent glazes for single-fired porous wall tiles by means of these diagrams, with the usual cooling cycles.

6. REFERENCES

(1) Rincón, J. "Separación de fases en vidrios". Ed. S.E.C.V. Madrid (1982)

(2) Vogel, W. "Chemistry of Glass". Ed. Am. Cer. Soc. U.S.A. (1985)

(3) "ASTM Standards on Color and Appearance Measurement" Ed. ASTM Philadelphia (1987)

(4) G. GEIRNAERT, Verres et Réfractaires, 21-30, 25(1) (1971)

(5) E. PLUMAT, Silicates Industriels; 5-13,1 (1967)

(6) L. PROD'HOMME, Verres Réfract., 604-613,22(6) (1968)