USING BORON AS AN AUXILIARY FLUX IN PORCELAIN TILE COMPOSITIONS

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1. INTRODUCTION

Boron compounds have been used in glass manufacture for over 700 years. However, their large-scale use was not possible until the discovery during the last century of large deposits in America, Turkey and Europe. At present, the use of boron oxide (B_2O_3) in ceramic and glass industries represents more than half of the world consumption of boron oxide, estimated at 1.5 million tons of B_2O_3 per year.

Boron oxide is present in large proportions in the formulation of numerous commercial glasses. It acts as a flux and network former, allowing the formulation of glasses with combinations of properties could otherwise not be obtained. Boron oxide plays a key role as a low temperature flux when the alkaline levels are limited by other properties. Thus, boron oxide reduces melting, transformation and vitrification temperature, but unlike sodium and potassium alkalis, yields glasses with high chemical resistance, low thermal expansion and low electrical conductivity. In ceramics, boron oxide facilitates glaze thermal expansion and melting temperature fit to the characteristics of the tile body. For this reason, boron oxide is widely used in frits yielding glazes for ceramic floor and wall tiles, as well as for tableware, besides playing a decisive role in the formulation of lead-free glazes.

Another important borate application is glass wool production for thermal and acoustic insulation. Other important uses are the production of reinforcing glass fibre, enamels, optical glass as well as different technical applications of borosilicate glasses for lighting, laboratories, medicine, kitchen utensils or LCD screens.

In view of the wide variety of boron applications, and since many of these applications are due to its fluxing effect, a study was undertaken in this work of the technical feasibility of using different boric raw materials as auxiliary fluxes in manufacturing low porosity ceramic bodies.

2. OBJECTIVES AND SCOPE

This study has two objectives:

- To determine how boron affects the properties of stoneware floor tile and porcelain tile bodies, and how it affects the different preparation process stages.
- To determine the influence of different types of boric raw materials on the behaviour and properties of porcelain tile compositions, on contributing the same quantity of boron.

3. EFFECT OF BORON ON THE BEHAVIOUR AND PROPERTIES OF FLOOR TILE BODIES

First, the effect was studied of the presence of boron on the behaviour and properties of the following different types of floor tile bodies: red-firing stoneware, white-firing stoneware and porcelain tile bodies.

The following aspects were tackled in this part of the study:

- suspension rheological behaviour
- behaviour during the pressing stage
- behaviour during firing
- evolution of the crystalline-phase content during firing

3.1. EXPERIMENTAL

3.1.1 Materials

Tables 1 to 3 show the body compositions involved (red and white firing floor tile and porcelain tile). The raw materials used in the compositions and the percentages involved are those usually employed in industry.

The raw material used for adding boron to the compositions was Hydroboracite H-44, whose stoichiometric composition is $CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$.

Raw material	Content (%)
Moró clay	34
Villar 1 clay	32
Villar 2 clay	32

***Table 1.** Red-firing stoneware composition PGR (wt%).*

Raw material	Content (%)
Teruel clay	30
English clay	20
Potassium sodium feldspar	30
Lepidolite	20

***Table 2.** White-firing stoneware composition PGB (wt%).*

Raw material	Content (%)
Ukrainian clay	50
Sodium feldspar	40
Feldspathic sand	10

***Table 3.** Porcelain tile composition GP (wt%).*

3.1.2 Experimental development

Conditioning the compositions and raw materials.

Two compositions were prepared for each body, one composition without hydroboracite and the other containing 0.90 wt% of this raw material.

Before preparing the compositions, some raw materials underwent pre-treatment. The clays were dry milled in a hammer mill with an output screen mesh of 1 mm, whereas the non-plastic raw materials were wet milled in a ball mill to a reject of 2% on a 75 μm mesh screen. The different raw materials were subsequently mixed, including hydroboracite, in the appropriate percentages (Tables 1 and 3) and then wet milled until the following rejects were obtained:

- red stoneware floor tile: 4-5% at 63 μm
- white stoneware floor tile: 2-3% at 63 μm
- porcelain tile: 1.0-1.5% at 40 μm

Rheological behaviour

The influence hydroboracite had on the rheological behaviour of spray-drying suspensions was studied by determining the deflocculation curves. To carry out this test, suspensions were made from the compositions, determining suspension viscosity on adding different amounts of deflocculant. The deflocculant mixture was made up of three parts sodium metasilicate (SMT) and one part sodium tripolyphosphate (STPP). The measuring instrument used was a Gallemkamp viscometer with a no. 30 torsion wire.

In these tests, the solids content of the suspensions was kept constant for each type of composition in order to obtain results that could be compared. The solids content values were 68% for the PGR compositions, 72% for the PGB compositions and 67% for the GP compositions.

Behaviour during the pressing stage

Composition behaviour during pressing was studied by determining the compaction diagrams. In order to determine these diagrams, cylindrical test specimens (about 6 mm thick, with a 4-cm diameter) were formed by uniaxial pressing, at a moisture content of 5.5 % (dry base) and different pressing pressures which varied according to the type of body.

The test specimens were dried to constant weight at 110°C in an electric laboratory oven with recirculating air. Bulk density was subsequently determined by the mercury immersion method.

Behaviour during the firing stage

Composition behaviour during firing was studied by preparing the vitrification diagrams. These diagrams were determined by keeping the compactness of the specimens constant for each type of composition, with a view to eliminating the influence of this variable.

Firing took place in an electric laboratory kiln with a fast firing cycle and 6-min residence at peak temperature. The heating rate was 25°C/min and cooling was carried out by forced convection.

Bulk density, linear shrinkage and water absorption were determined on the fired specimens. Bulk density was determined by the mercury immersion method. Firing shrinkage was assessed as the difference between dry and fired specimen diameter and water absorption was determined by measuring specimen weight gain after immersion for two hours in boiling water.

Evolution of crystalline phases during firing

To study the effect the presence of boron had on the evolution of the crystalline phases during firing, 9.5 wt% of Hydroboracite was added to the porcelain tile composition. This percentage was chosen in order to show up the effect more clearly.

Test specimens were pressed and fired from this new composition referenced as GPHB, following the procedures above. Test specimens were also prepared from the composition without hydroboracite (GP) in order to have reference specimens.

The fired specimens were milled and X-ray diffraction (XRD) scans were subsequently run. Scans were also performed on green specimens with a view to determining starting crystalline-phase proportions.

The crystalline phases present in each of the samples were identified by comparing the diffractograms with the JCPDS files for pure crystalline phases. To study the evolution of the crystalline phases in the samples with firing temperature, a peak deconvolution and integration software was used to calculate integrated peak intensity of the strongest line. The peaks with the greatest relative intensity were chosen for quartz (d=3.34Å) and albite (d=3.19Å). A peak of lower relative intensity was chosen for mullite (peak d=5.39Å), as this did not present overlapping with peaks from other phases.

3.2 RESULTS OBTAINED AND DISCUSSION

Rheological behaviour

Figures 1, 2 and 3 show the influence of hydroboracite on the behaviour of the compositions during the deflocculation stage. As already mentioned, in this series of tests the suspension solids content was kept constant for each type of composition.

It can be observed that the addition of hydroboracite to the three types of compositions shifted the curves towards higher deflocculant contents, therefore requiring more hydroboracite to achieve working viscosity. This effect appeared to be more pronounced in the white body compositions, as in these compositions it was necessary to raise the amount of deflocculant by 0.5%, whereas the deflocculant increase for the red body compositions was only 0.2%. On the other hand, it is worth pointing out that the addition of hydroboracite did not modify the value of the minimum viscosity obtained, thus keeping suspension solids content constant and hence holding spray-drying efficiency.

The modification of the rheological behaviour of the suspensions on adding hydroboracite is due to the partial solubility of this raw material in aqueous medium. This solubility raised Ca^{++} and Mg^{++} ion concentrations in the solution, as well as boron ion concentration in different states of hydration. While the Ca^{++} and Mg^{++} ions acted as flocculants [1], therefore requiring the addition of a greater quantity of deflocculant (fundamentally tripolyphosphate) to capture and/or complex these [2], the boron ion did not have any negative effect on the rheological behaviour of the suspensions [3,4].

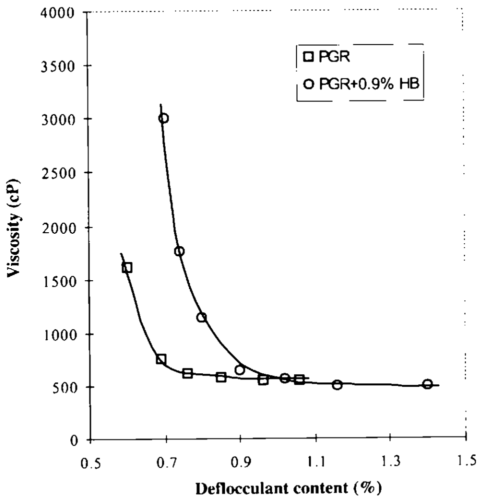

***Figure 1.** Deflocculation curves of the red body compositions.*

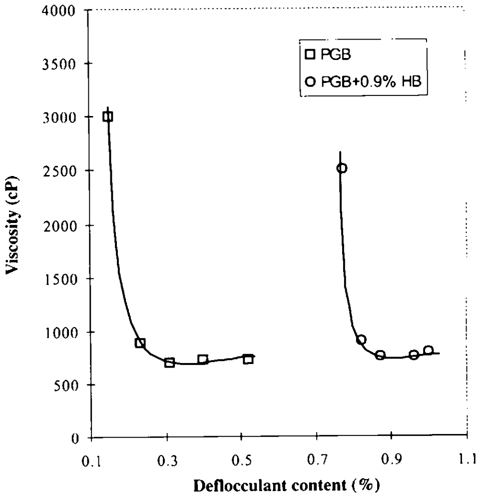

***Figure 2.** Deflocculation curves of the white body compositions.*

Behaviour during the pressing stage

Fig. 4 plots the compaction diagrams of the different compositions. Bulk density rose in all the studied compositions as applied pressure increased, the experimental data fitting a straight line when plotted on semi-logarithmic scales. This is standard behaviour in these types of compositions.

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[1] PUGH, R.J.; BERGSTROM, L. *Surface and colloid chemistry in advanced ceramics processing.* New York: Marcel Dekker, 1994.

[2] REED, J.S. *Principles of ceramic processing.* 2nd ed. New York: John Wiley, 1995.

[3] HOWLES; J.A. *Effects of Boron Compound Incorporation into a Whiteware Body,* February, 1999, masters thesis, Alfred University, pp 14-31Carty

[4] ROSSINGTON, K.R.; CARTY, W.M. *The Effects of Ionic Concentration on the Viscosity of a Clay-Based System;* 1998, Ceramic Engineering Science Proceedings, vol 19, no. 2., pp 65-76.

From the analysis of these diagrams it can be inferred that although the addition of Hydroboracite slightly lowered specimen compactness, very few differences were detected owing to the low proportion of this raw material in the compositions.

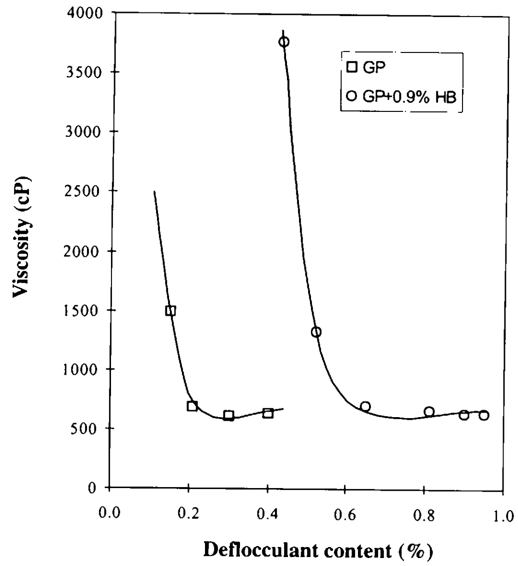

Figure 3. Deflocculation curves of the porcelain tile compositions.

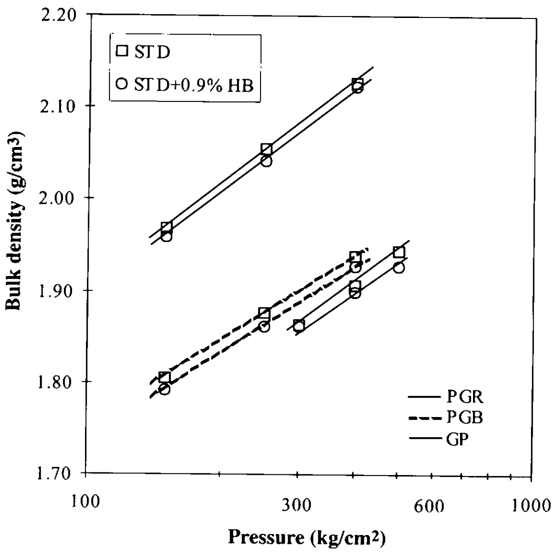

Figure 4. Compaction diagrams.

Behaviour during the firing stage

Figs. 5, 6 and 7 present the vitrification diagrams of the compositions. In these diagrams the evolution of linear shrinkage and water absorption with firing temperature has been plotted for the two floor tile compositions, whereas for the porcelain tile, the plot is shown of specimen bulk density versus water absorption.

For the three types of compositions the curves shifted towards lower temperatures on adding hydroboracite, indicating that this raw material raised the fluxing character of the compositions and therefore allows the firing temperature for these products to be reduced.

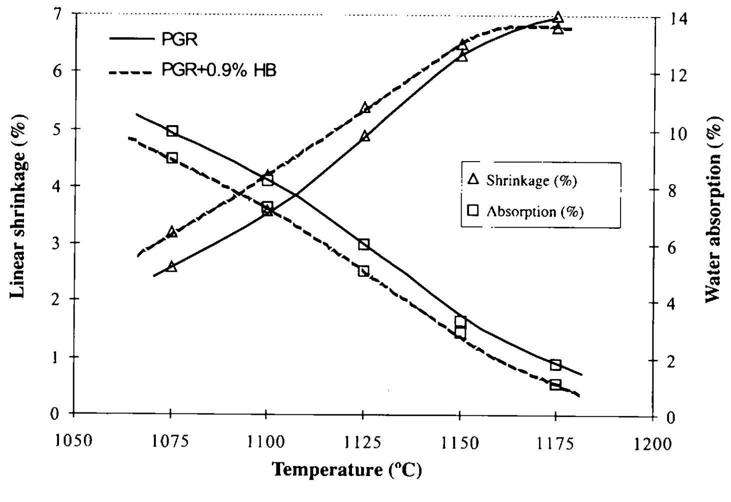

Figure 5. Vitrification diagrams of the red-firing stoneware floor tile compositions.

These diagrams were used to calculate the firing temperature at which the floor tile specimens attained working water absorption. A value of 4% water absorption (WA) was adopted for the red-firing compositions (T_4) and a value of 2% for the white-firing compositions (T_2). Specimen properties were then calculated at these firing temperatures: linear shrinkage (LS) and bulk density (Dap). Tables 4 and 5 set out the results. The tables also include the shrinkage-temperature curve slopes ($\Delta LS/\Delta T$) at working temperature, due to their close connection to the robustness of the compositions regarding sizes and rectangularity._

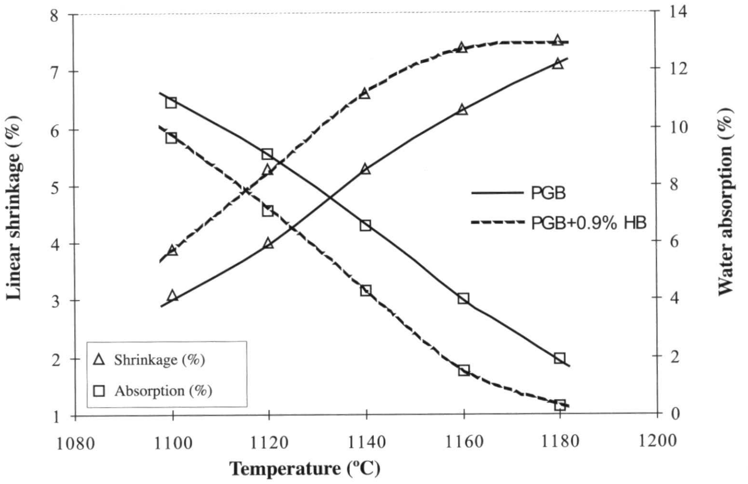

Figure 6. *Vitrification diagrams of the white-firing stoneware floor tile compositions.*

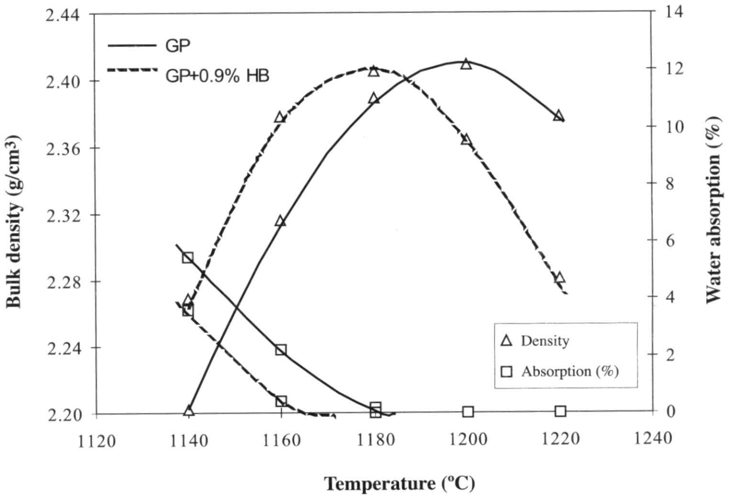

Figure 7. *Vitrification diagrams of the porcelain tile compositions.*

	T_4 (°C)	WA (%)	LS (%)	Dap (g/cm^3)	($\Delta LS/\Delta T$)
PGR	1143	4.0	6.0	2.350	0.055
PGR+0.90 HB	1137	4.0	6.0	2.336	0.045

Table 4. *Properties of the red-firing stoneware floor tile compositions with 4% water absorption.*

	T_2 (°C)	WA (%)	LS (%)	Dap (g/cm^3)	($\Delta LS/\Delta T$)
PGB	1179	2.0	7.1	2.292	0.031
PGB+0.90 HB	1155	2.0	7.3	2.284	0.027

Table 5. *Properties of the white-firing stoneware floor tile compositions with 2% water absorption.*

It can be observed that for both products, adding hydroboracite lowered the temperature at which working water absorption was reached, the drop depending on the type of product involved. The red-firing composition temperature decreased by about 6°C, whereas for the white body compositions the reduction was much higher, between 20 and 25°C.

The reason why the presence of hydroboracite in the compositions lowered specimen firing temperature was because of the low melting point of this raw material, which reduces the temperature at which the first liquid phases start to form. This, together with the lower viscosity provided by the presence of boron in the liquid phase [5], raised the specimen vitrification rate, thus reaching a given porosity at lower temperatures.

The increase in composition meltability did not significantly raise specimen shrinkage or the shrinkage-temperature curve slopes ($\Delta LS/\Delta T$) as can be inferred from Tables 4 and 5. This indicates that the addition of hydroboracite at the tested percentages did not alter size stability of the specimens (the tendency of size and rectangularity problems to appear).

For the porcelain tile compositions, the temperature at which maximum densification (T_{max}) was reached was taken as the working temperature. The value of this temperature and the properties corresponding to the porcelain tile specimens are presented in Table 6. It can be observed that the hydroboracite addition lowered the working temperature by about 20 °C, without appreciably modifying specimen shrinkage or porosity, whether apparent or closed. In principle, this suggests that the stain resistance of the polished specimens should not deteriorate on adding hydroboracite at the tested percentage.

It should be pointed out that the firing range (I) in which the specimens present minimum porosity for the amount of hydroboracite added (0.9 %) barely decreased. This parameter was calculated as the temperature range in which the specimen bulk density is held without decreasing more than 0.01 g/cm^3 in relation to the maximum.

	T_{max} (°C)	WA (%)	LS (%)	Dap (g/cm^3)	PI*10^5 (cm^{-1})	I (°C)
GP	1198	0.0	7.8	2.410	3.6	24
GP+0.90 HB	1178	0.0	7.9	2.406	5.1	22

Table 6. *Porcelain tile specimen properties at maximum densification temperatures.*

Evolution of crystalline phases

The following phases were identified in the green specimens: illite, kaolinite, quartz and albite. The peaks corresponding to hydroboracite were not detected in the diffractogram corresponding to the GPHB composition. This would probably be due to the X-ray absorption effect, as the hydroboracite coefficient of mass absorption is much lower than that of the matrix in which it is found.

The reflection intensity (peaks) of a crystalline phase in a sample depends on the relative concentration of the phase in the sample. This relation is seldom linear, but for samples with the same characteristics (similar samples), carrying out the diffraction tests under the same conditions, each crystalline-phase content can be compared in the different samples from the peak intensity values of the phase involved.

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[5] BRÜCKNER; FERNÁNDEZ, J. M. *Physikalisch-chemische untersuchugen in system* B_2O_3-SiO_2. Glastechn. Ber. 39. (1966) 6, 283-293.

Only quartz, albite and mullite were detected in the fired specimens. The peaks corresponding to the clay minerals (illite and kaolinite) were not detected owing to the decomposition that these minerals undergo at relatively low temperatures (<1000 °C).

It can be observed in Figure 8 that sodium feldspar (albite) gradually melted during the firing of the porcelain tile (GP) at high temperatures (>1000 °C), forming a liquid phase, until it practically disappeared in the composition at 1200 °C. Quartz also dissolved at a slower rate (curve slope) than albite. However, the quartz dissolution rate increased at high temperatures owing to the rise in liquid-phase content and decrease in viscosity, which facilitated dissolution. Mullite was also formed in rising proportions at the tested temperatures.

The addition of hydroboracite to the composition lowered quartz and albite content in the whole temperature range, indicating a considerable rise in the dissolution rate of these minerals. After the mullite formed, it was found to re-dissolve progressively. These differences stem from B_2O_3 forming a low viscosity glass that favours dissolution of the crystalline phases contained in the specimens.

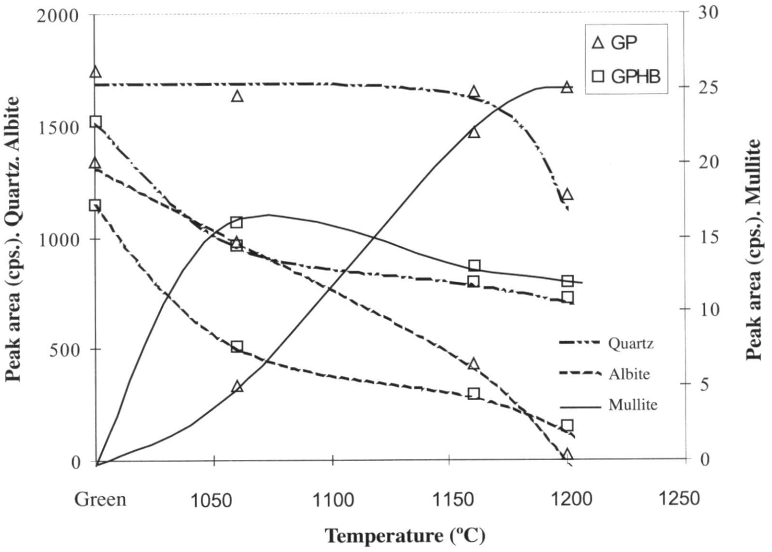

Figure 8. *Variation of crystalline phase content with firing temperature.*

Therefore, although the addition of B_2O_3 did not modify the crystalline phases existing in the fired product, it varied their proportions. Table 7 shows the peak areas corresponding to the phases detected at each composition's working temperature, 1198°C for the GP composition and 1084°C for the GPHB composition. The table shows that the presence of boron in the starting composition reduced the amount of quartz and mullite due to the capability of the formed liquid phase to dissolve both minerals in the melt. On the other hand, the content in albite is higher, which appears to indicate that this mineral integrates predominately in the melt by a gradual melting mechanism rather than a dissolution mechanism.

	GP (1198°C)	GPHB (1084 °C)
Quartz	1190	880
Albite	25	400
Mullite	24	16

Table 7. *Fired specimen peak areas at maximum densification temperature.*

4. INFLUENCE OF THE BORIC RAW MATERIALS ON PORCELAIN TILE COMPOSITION BEHAVIOUR AND PROPERTIES

In the previous section it was observed that adding small quantities of boron, in the form of hydroboracite to the low porosity body compositions increased the specimen vitrification rate, without deteriorating its dimensional stability. Therefore, the fluxing effect of boron can be used to modify the firing cycles, by either decreasing peak temperatures or reducing specimen residence time at high temperatures.

The addition of hydroboracite required significantly raising the amount of deflocculant needed to keep spray-drying suspension viscosity unchanged, owing to the solubility of the flocculating alkaline-earth ions (Ca^{++} and Mg^{++}) in aqueous medium. For this reason, in this part of the work it was decided to study the effect of the nature of the boron-contributing raw materials on porcelain tile composition (GP) behaviour and properties, paying special attention to suspension rheology.

4.1 EXPERIMENTAL

4.1.1 Materials

The porcelain tile composition used in this part of the study is described in point 3.1.1 (GP). The following boron-contributing raw materials were used: Hydroboracite, Borax and Boric acid. These raw materials present different degrees of solubility in water and besides boron, they also provide the composition with other cations. Table 8 presents some of their characteristics.

	Boric acid (AB)	Hydroboracite (HB)	Borax (BX)
Molecular formula	H_3BO_3	$CaO{\cdot}MgO{\cdot}3B_2O_3{\cdot}6H_2O$	$Na_2O{\cdot}2B_2O_3{\cdot}5H_2O$

Table 8. *Stoichiometric composition of the boric raw materials.*

4.1.2 Experimental Procedure

Composition preparation

Two series of compositions were prepared from porcelain tile composition GP. In the first series, the boric raw material addition to the compositions was the amount required by each boric material to provide the composition with 5% B_2O_3, whereas in the second series the B_2O_3 content was 1.0%. The composition reference is made up as follows: type of composition (GP), amount of B_2O_3 (0.5 or 1.0) in the composition and boron-contributing raw material (AB, HB or BX). The methods used for preparing the compositions are set out in point 3.1.2.

Rheological behaviour

The suspensions were prepared by dissolving and/or dispersing the boric raw material in water, adding the deflocculant and finally the composition. All the suspensions were prepared with a solids content of 67 wt% with a 0.3% deflocculant content. The deflocculant used was a mixture of metasilicate and sodium tripolyphosphate.

The rheological parameters were measured on a Bohlin CS-50 rheometer, controlling the applied torque, and continuously measuring the arising strain.

The flow tests consisted of the following series of stages:

1° Stirring at high shear rates for 30 seconds.
2° Rest for 300 seconds.
3° Rising shear stress ramp
(stabilisation = 30 s, integration = 10 s).
4° Falling shear stress ramp (ídem).

Finally, in order to determine whether there was any evolution of rheological properties on ageing, the suspensions were stored for 4 days, after which the flow curves were determined again following the procedure indicated above.

Firing behaviour during firing

The evolution of bulk density, linear shrinkage and water absorption with temperature was determined according to the procedures described in point 3.1.2. Not only were these properties assessed, but also the specimen tendency to deform pyroplastically. Prism-shaped test specimens were made for this purpose measuring 80 mm long, 20 mm wide and 7 mm thick and subsequently fired, only supported at their two ends to allow them to deform during firing. The pyroplasticity index (PI) as calculated by means of the following equation:

$$PI = \frac{4 \cdot e^2 \cdot s}{3 \cdot L^4}$$

where:

e: specimen thickness
s: sag
L: span between supports

Finished product properties

Two fired specimen properties were determined: colour and stain resistance of the polished product.

The chromatic coordinates (L*, a*, b*) were determined on a diffuse reflectance spectrophotometer, using a D_{65} type light source and standard observer at 10°.

Before assessing stain resistance, the fired specimens were polished with progressively finer-grained abrasive, first with silicon carbide, then by diamond lapping and finally with an abrasive with a mean grain size of 1 μm.

The chromatic coordinates of these specimens were determined. They were subsequently impregnated with black ink using a xylene-free, indelible felt-tipped pen. After 60 seconds the specimens were subjected to cleaning with a white, fibre, Scotch-Brite scouring pad, soaked in alcohol, set on a head fitted to a device that rotated at 250 r.p.m., exerting a force of 10 kg. The cleaning process lasted 10 min, after which the chromatic coordinates were determined again. Stain resistance was assessed as the difference between coordinate L* before and after cleaning. The difference was calculated at a temperature slightly above maximum densification temperature.

4.2 RESULTS AND DISCUSSION

4.2.1 Rheological behaviour

Figure 9 presents the variation of viscosity with shear rate, measured 60 min after composition preparation. It can be observed that the nature and content of the boric raw material had a marked effect on suspension rheological behaviour. However, while the boric acid addition did not produce any significant changes when the B_2O_3 content was 0.5%, the addition of boric acid containing greater percentages of this raw material (1.0 de B_2O_3) slightly increased viscosity. The presence of hydroboracite and borax also led to higher suspension viscosity, especially borax, with yielded viscosity values exceeding the instrument´s measurement range, which is why the values are not shown in Figure 9.

In order to observe this effect more closely, the viscosity of these suspensions was calculated at a shear rate of 0.1 s^{-1}. It was found that the GP and GP+0.5AB suspensions respectively gave rise to viscosities of 125 and 140 Pa·s. The viscosity produced by the other compositions was higher, ranging from 290 Pa·s for the GP+1.0AB composition to 870 and 1340 Pa·s for the GP+0.5HB and GP+1.0HB compositions.

Figure 10 depicts the behaviour of these suspensions after standing for 4 days. Only the curves corresponding to the reference suspensions (GP) and with boric acid are shown, because the viscosity of the remaining suspensions exceeded the instrument´s measuring range. The figure shows that the presence of small percentages of boric acid (0.5 % B_2O_3) did not negatively affect suspension stability on ageing. Greater percentages of this raw material appear to slightly raise suspension viscosity after a 4-day stand.

It can therefore be inferred that boric acid, in percentages of 0.9 % (equivalent to 0.5 wt% B_2O_3), is the only raw material that allows adding boron without having a negative effect on porcelain tile suspension rheological behaviour. For this reason, the remaining part of the study was carried out with this raw material only.

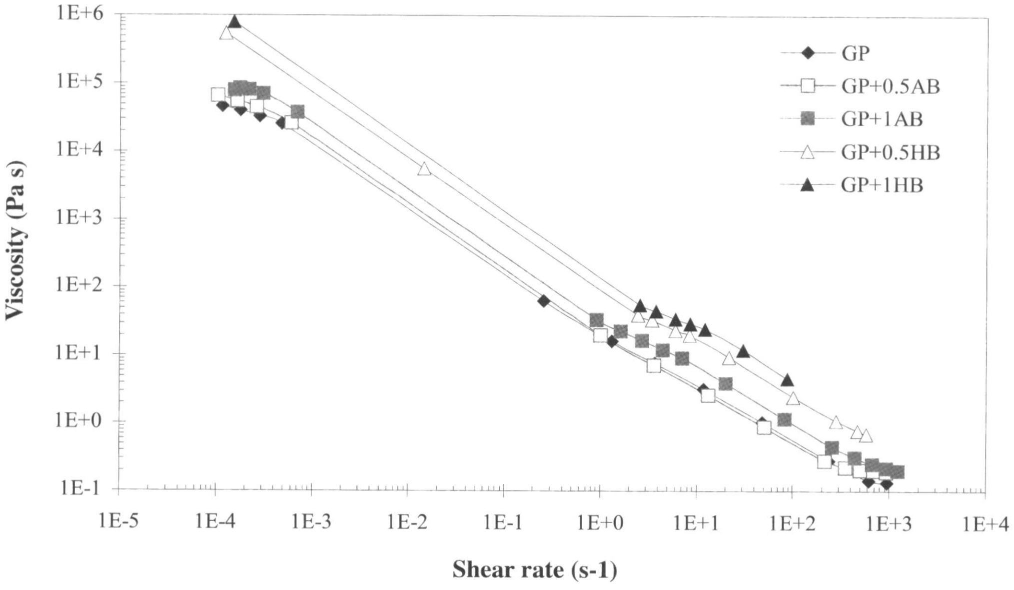

Figure 9. *Viscosity variation with shear rate of recently prepared suspensions.*

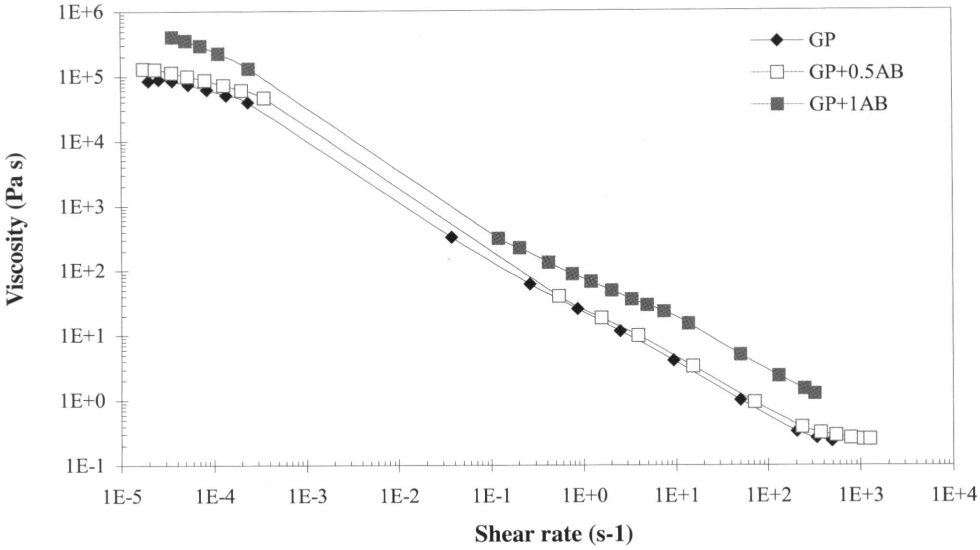

Figure 10. Viscosity variation with shear rate of the compositions after 4 days.

4.2.2 Firing behaviour

Figure 11 shows the evolution of bulk density and water absorption with peak firing temperature. It can be observed that adding boric acid produced two effects. On the one hand, it shifted the curves towards lower temperatures. This effect was more pronounced on raising the amount of boric acid. On the other hand, it lowered the peak bulk density reached at a 1.0% B_2O_3 content.

Table 9 list specimen properties at maximum densification temperature. It was found that adding 0.5% and 1.0% B_2O_3 to the composition lowered the working temperature by 15°C and 28°C respectively. The addition of 0.5% B_2O_3 did not modify the porosity of the fired product, whereas a 1.0% addition increased specimen closed porosity, detected from the decreased fired specimen bulk density. To verify this, specimen cross sections at maximum densification were observed by optical microscopy, shown in Figure 12. Adding 0.5% B_2O_3 did not produce any significant changes in the specimen internal microstructure, whereas the addition of 1.0% B_2O_3 modified the microstructure substantially. The most important changes lay in an increased pore-size and pore-occupied area, as well as greater pore sphericity, characteristics indicating a higher quantity of liquid phase with a lower viscosity.

This last feature produced a slightly higher tendency to pyroplastic deformation in the specimens containing 0.5% B_2O_3 than in the GP composition.

	GP	GP+0.5AB	GP+1.0AB
T_{max} (°C)	1198	1183	1170
LS_{max} (%)	8.1	8.0	7.9
Dap_{max} (g/cm^3)	2.410	2.412	2.388
WA_{max} (%)	0.0	0.1	0.0
PI	4.2	5.0	-

Table 9. *Fired specimen properties at maximum densification temperature.*

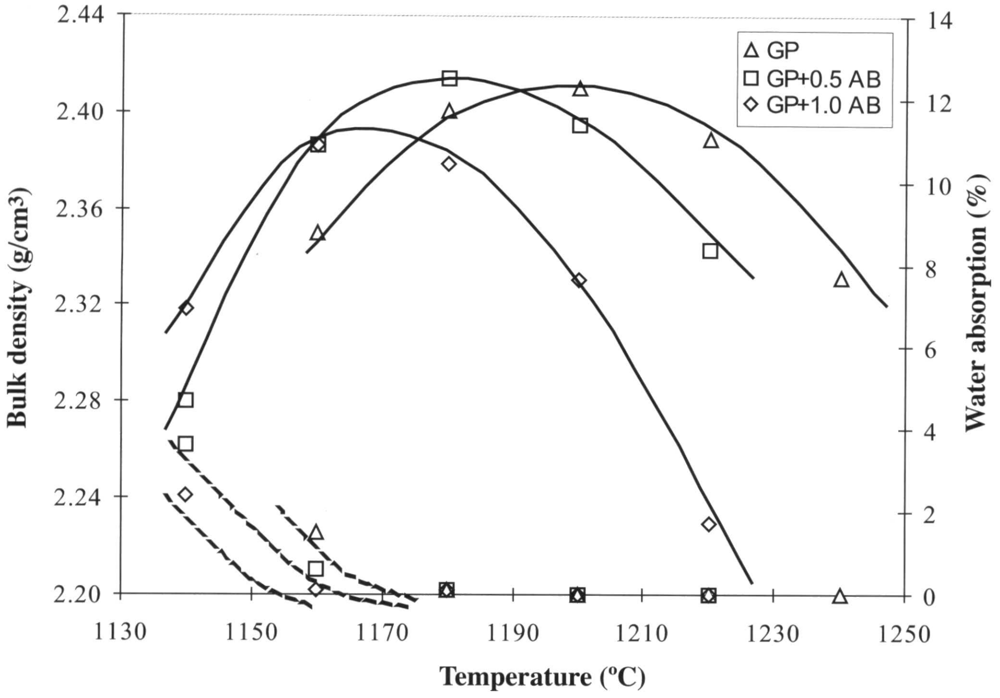

Figure 11. Vitrification diagrams.

4.2.3 Finished product properties

Table 10 sets out the values of the chromatic coordinates and ΔE* of the specimens at maximum densification temperature. It can be observed that the boric acid addition did not appreciably alter fired specimen colour or the stain resistance of the polished specimen with an 0.5% B_2O_3 addition. This last characteristic matches the microstructural observations performed in the previous section, where no significant changes were observed on adding 0.5% B_2O_3.

	GP	GP+0.5AB	GP+1.0AB
L*	74.9	75.1	75.2
a*	1.9	1.9	1.9
b*	12.5	12.5	12.6
ΔE*	2.2	2.1	-

Table 10. *Fired product properties at maximum densification temperature.*

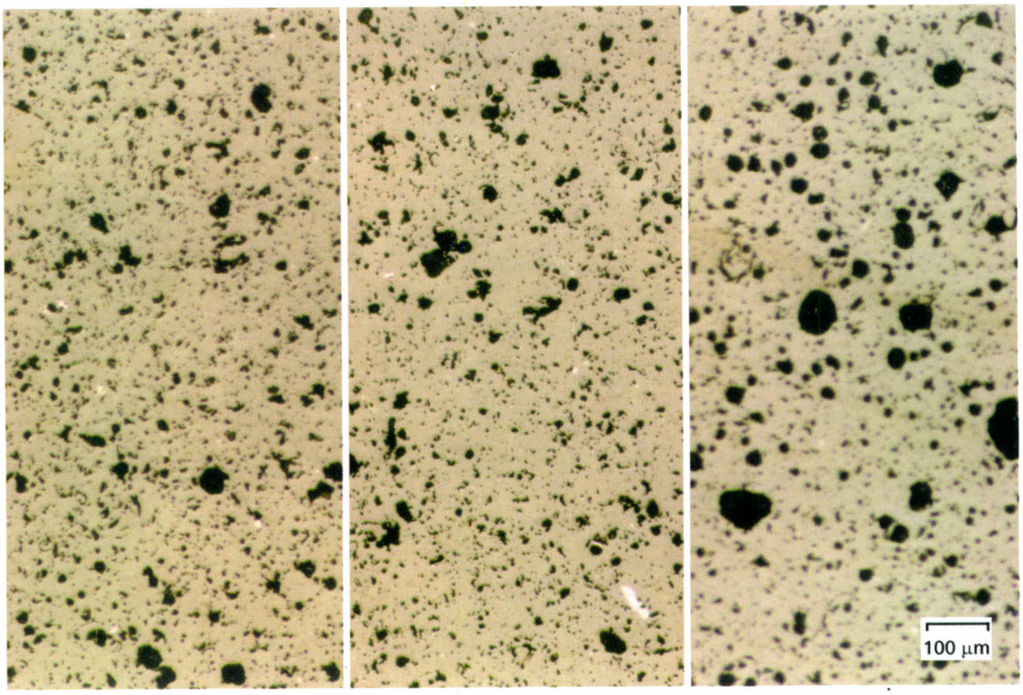

Figure 12. Specimen microstructure at maximum densification.

5. CONCLUSIONS

The following conclusions were drawn from the results obtained in this study:

- The presence of small quantities of B_2O_3 in the compositions used for obtaining low porosity bodies increased the tile vitrification rate. This could be used to either reduce the peak firing temperature of these products or lower tile residence time at high temperatures. The fluxing effect is due to the low melting point exhibited by the boric compounds.

- The introduction of small amounts of boric raw materials did not significantly modify composition behaviour during pressing nor the robustness of the materials with regard to the appearance of dimensional stability defects (sizes and rectangularity).

- The nature of the boron-contributing raw material had a pronounced effect on suspension rheological behaviour. In this study it was observed that while the use of Hydroboracite and Borax made porcelain tile suspension processing more difficult, using boric acid in quantities up to 0.9% (0.5% B_2O_3) did not alter suspension rheology.

- The use of boric acid in the indicated amounts (0.5% B_2O_3) did not affect tile behaviour during the different manufacturing process stages or worsen the technical properties of the fired product. It can therefore be concluded that boric acid can be used as an auxiliary flux in porcelain stoneware compositions.