STUDY OF THE BONDING OF UNFIRED GLAZE LAYERS (*)

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ABSTRACT

This study addressed the bonding between layers of glaze, engobe and body in single-fired ceramic wall tile, in order to obtain information that might help to solve problems relating to bonding.

A series of experiments was designed for this purpose with materials that were applied according to the usual industrial method. Measurements were performed in the laboratory, with an assembly that allowed the resistance to the deformation force to which the glaze and engobe layers were subjected, to be recorded. The results were related to the bonding of the above materials.

1. INTRODUCTION

The bonding that develops between different layers of glaze, glaze and engobe, and engobe and body in fired ceramic pieces, stems from the interfaces arising during firing. These interfaces relate directly to the nature of glazes and body, to the type of firing, and also to the application system used. When these glaze layers are still unfired, in the prefiring stages, they require a minimum strength, as the pieces must withstand a series of mechanical transportations, as well as different decorating operations, cleaning or finishing. During drying of the ware, after glazing, and during the first firing stages, changes in curvature and dimensions also take place. The stresses arising in these stages must be absorbed and withstood by the ware, in order to prevent defects from developing.

The mechanical strength of the green clay body plays a decisive role in keeping fractures or cracks from arising in these stages, but the cohesion and bonding between the layers will determine

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if they do or do not successfully withstand the mechanical stresses the pieces must undergo in the operations mentioned above.

Cohesion and bonding of the glazes depend to a large extent on the properties of their component particles: nature, size distribution, shape and texture, as well as their possible surface impurities. Cohesion and bonding also depend upon the presence of binders, moisture content, rheological parameters, and the conditions under which the glazing operation is carried out.

2. OBJECTIVES

A study was undertaken of the bonding between unfired glaze, engobe and body by measuring the force required to make a blade penetrate the layers, until fracture and separation took place.

The objective was to obtain a quantitative measurement that is directly related to bonding. Thus, the bonding strength of different materials, and its evolution in function of some of the most commonly utilized variables in industrial practice could be comparatively studied.

It is attempted to relate the measurements performed to some commonly observed facts in practice, in order to thus confirm the validity of the method and justify its application in studying problems involving bonding.

3. MATERIALS

3.1 DESCRIPTION

The process selected for the study was single-fired ceramic wall tile manufacture, with characteristic process materials, using two engobe and two glaze compositions.

The engobes have the same composition, but differ as to the nature of the binder employed. Carboxymethyl cellulose (CMC) was used in one, while sodium bentonite was employed in the other, both being widely used in the industry.

A crystalline and a white glaze were selected, both obtained from frit ground with kaolin, using CMC as a binder and sodium hexametaphosphate as a deflocculant.

The body used involved green pieces sized 20x30 cm, which had been industrially fabricated.

The materials were referenced as follows:

CMC engobe	EC
Bentonite engobe	EB
Crystalline glaze	CP
White glaze	BP

All the slips used were prepared in 200 kg ball mills with high density alumina lining. The engobes were milled to a reject of 1% on a 44 micron screen aperture. The glazes were prepared at a 4% reject except in those cases in which different values were studied.

Bulk density of the body used was 2.03 g/cm^3 except where other values were studied.

Application was carried out in a laboratory glazing machine, simulating the usual industrial bell-glazing application, both for engobe and glaze.

Except in those cases in which other values were studied, the application was 500 g/m^2 by weight difference for the engobe, and 1125 g/m^2 by weight difference for the glazes.

Engobe density was 1.86 g/cm^3 and glaze density was 1.80 g/cm^3. The viscosities were variable, depending on the modifications effected for the study.

3.2 VARIATIONS PERFOMED

A first characterization of the layers obtained was performed with engobes EC and EB, and glazes CP and BP, individually applied as well as in combinations of the two engobes and the two glazes. The effect of the composition and process variables was then studied, using the materials detailed in Table 1, which were prepared and applied as described above. The modified variable and the direction of the modification are also shown.

Table 1.

Material	Variable	Direction
EC-1	Amount of CMC	-
EC-2	Amount of CMC	+
EB-1	Amount of bentonite	-
EB-2	Amount of bentonite	+
BP-1	Amount of CMC	-
BP-2	Amount of CMC	+
BP-3	Amount of CMC	- -
BP-4	Particle size	-
BP-5	Particle size	+
BP	Amount of applied glaze	-
BP	Amount of applied glaze	+
BP	Compaction of the body	-
BP	Compaction of the body	+
BP-6	CMC viscosity	-

In those cases in which the engobe was modified, the same reference glaze was always applied to it. When the modification involved the glaze, the same reference engobe was always used.

4. EXPERIMENTAL PROCEDURE

Bonding and cohesion of the engobe and glaze layers were measured on three test pieces obtained from industrially applied pieces. A universal testing machine was used, fitted out with the assembly required to carry out the measurements (Figure 1).

The test involves three clearly differentiated steps:

1. In the first step, a blade joined to a load cell by a rod (Figure 2.1), starts penetrating the test material, under the thrust of a vertically travelling crosshead (Figure 2.2). This allows the force required to cut into the layers to be recorded, in function of the distance travelled by the blade. This force is related to the cohesion and bonding between the layers.
2. In the second step, when the blade has penetrated, there comes a moment at which the force exerted is greater than the bond strength between the layers, making them fracture and separate (Figure 2.3).

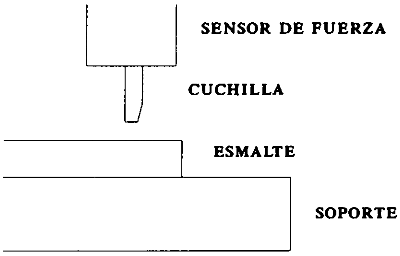

Figure 1. Schematic of the experimental assembly used

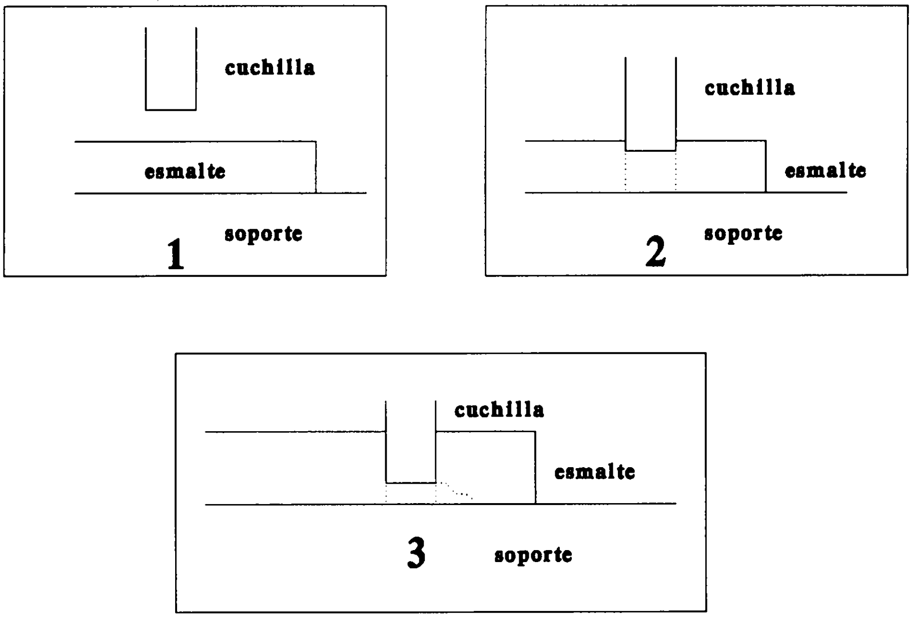

Figure 2. Schematic of layer fracture

* *Figures 1 and 2: Sensor de fuerza = Force sensor; Cuchilla = Blande; Esmalte = Glaze; Soporte = Body.*

3. In the third step, the blade continues to penetrate, concurrently applying a deformation force. If the fracture in the previous step took place in the first moments of blade penetration, a certain thickness of the fractured layer may have remained joined to the following layer. If this joined film is sufficiently thick, a second fracture might arise when enough force is achieved to separate the layers. However, if the film is very thin, it will be compressed by the deformation force being exerted and the blade will pass through in a continuous movement and enter the following layer. A new cycle then commences, if there are subsequent layers, or the blade simply penetrates the body if one sole layer is involved.

The results of the force recorded are plotted versus blade displacement in the layers.

5. RESULTS AND DISCUSSION

5.1 BONDING AND COHESION OF UNFIRED COATINGS OF ONE LAYER (ENGOBE OR GLAZE)

Figure 3 shows the results of the tests performed on solely applying engobe layers to the body. The displacement of the crosshead of the measuring device as the blade enters the test piece is plotted on the abscissa. The ordinate axis shows the value of the force with which the layer resists penetration. The peaks observed in the area approaching 0.2 mm, correspond to the moment of layer fracture, that is, the moment at which the value of the force is reached, which is required to separate the layer from the body. The value approaching 0.2 mm, coincides precisely with the thickness of the applied unfired engobe layer.

The force required to cause fracture is clearly smaller in the case of engobe EC (whose composition included CMC) than engobe EB (which contained bentonite).

Figure 4 plots the data of the test with the CP crystalline and BP white glaze on the body. The force values are quite similar in both cases, which indicates not very significant differences in layer cohesion. There is a fracture peak in the first few moments of blade displacement, followed by a not very significant increase in force, until a displacement of about 0.5 mm is reached, corresponding to the thickness of the applied unfired layers. There is then a marked, although continuous, change, in the slope of the curves when the blade reaches the body. This corresponds to the typical test steps described above. The existence of a fracture peak in the first instants of layer penetration, indicates greater brittleness and less cohesion in the glaze layers than in the engobe layers.

The domain between 0.1 and 0.5 mm is virtually a straight line with a very slight slope, in which force increases slightly. This indicates that the blade encounters little resistance during a certain interval in its travel, as the glaze film that remains after fracture has fissures and pores owing to the damage arising from the fracture.

The lack of a fracture peak close to the glaze-body interface, indicates that the film that remains after the first fracture is thin and does not fracture again.

Thus, on comparing the plots of Figure 4 with those of Figure 3, a difference in the forces can be observed, in favour of the engobes, as was expected. Incorporating clays into the engobes tends to favour some factors that raise these forces (high specific surface area, interparticle interaction, etc.).

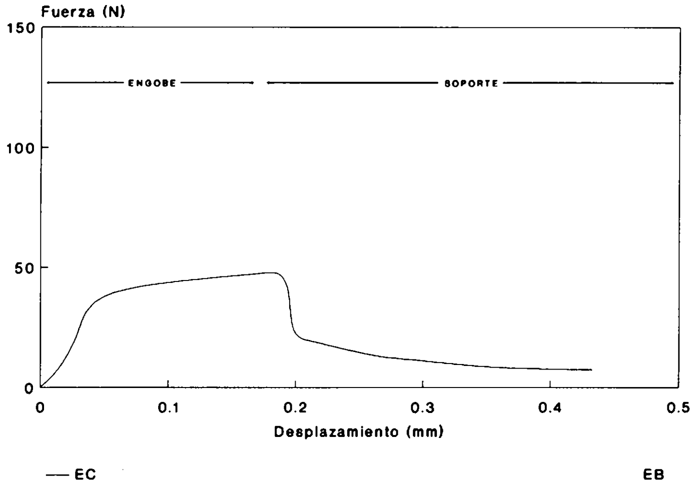

Figure 3. *EC and EB engobe bond*

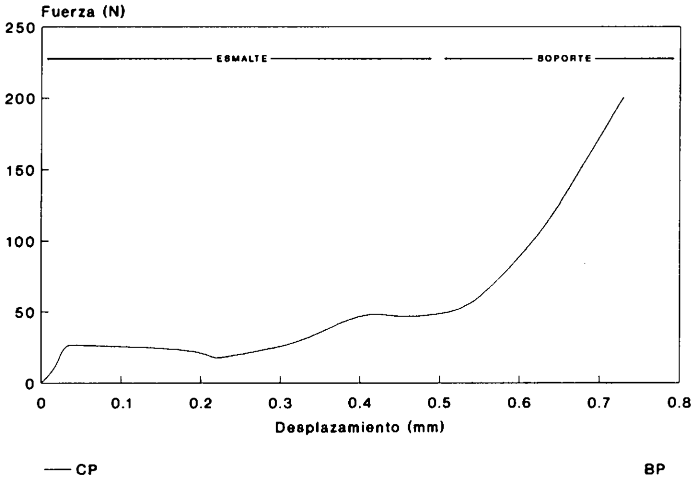

Figure 4. *CP crystalline glaze and BP white glaze bond*

5.1.1 Ageing

After storing the engobes and glazes that were prepared for quite some time to age them, they were applied again. The findings are reported in Figs. 5 and 6. Once again, the EB engobe exhibits very high force values while the EC engobe presents considerably lower values. The curves obtained with the glazes exhibit quite similar behaviour to when they were applied freshly ground, which indicates little change in bond strength of these layers with ageing.

5.2 BONDING AND COHESION OF TWO-LAYER UNFIRED COATINGS (ENGOGE AND GLAZE)

The superimposed application of glaze on engobe, as is usually effected in industrial manufacture, does not give rise to significant modifications in the behaviour of the layers with regard to what had been observed on performing the bond test with each individually. Figure 7 plots the curves corresponding to the crystalline glaze CP and the white glaze BP, applied on engobe EC (with CMC). A first stretch can be observed with the characteristic curve shape for the glaze layer. There is a peak corresponding to a first fracture close to the surface (the first moments when the blade penetrates the glaze), and another corresponding to a second fracture, near the engobe interface domain. The second interval corresponds to the deformation the engobe layer undergoes and also resembles the curve obtained on applying it individually. The force then quickly climbs to a new peak, which indicates fracture in the proximity of the body.

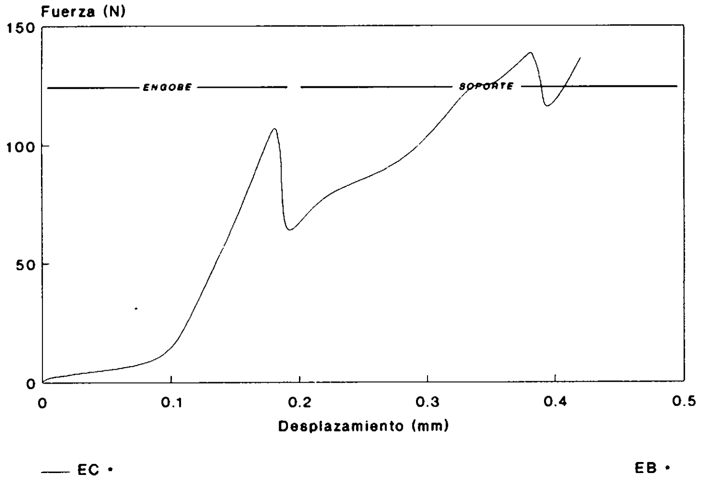

Figure 5. *EC and EB engobe layer bond obtained from the corresponding aged suspensions*

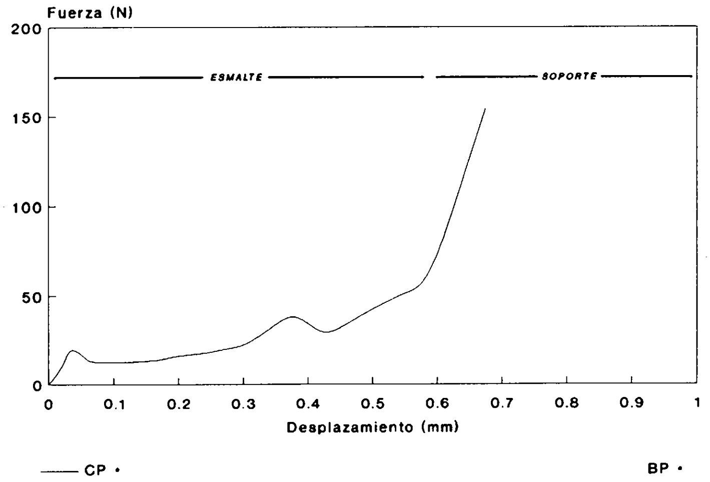

Figure 6. *CP and BP glaze layer bond obtained from the corresponding aged suspensions*

In the tests performed with glaze layers applied onto engobe EB (Figure 8), the areas corresponding to glaze and engobe can also be appreciated. The difference with the former case (Figure 7) lies in the fact that the forces recorded in the engobe area are larger, as had already been observed (Figure 3).

* ***Other figures:*** *Fuerza = Force; Desplazamiento = Displacement; Engobe = Engobe; Soporte = Body; Esmalte = Glaze.*

However, different behaviour was observed when the additive used was bentonite (engobes EB, EB-1 and EB-2). The results are depicted in Figure 12. The increase in the amount of bentonite (EB-2) was not observed to improve the properties of the layer that was formed. However, a decrease in this additive (EB-1) gave rise to a notable drop in cohesion and bonding of the layer.

It can be stated, on comparing the two types of studied engobes, that the EC engobe has less bonding strength than engobe EB. The former exhibits greater stability in the face of possible variations in binder content, while the latter is highly affected by a drop in the amount of bentonite, which indicates that a more sensitive material is involved, requiring suitable control of the proportioning of this raw material.

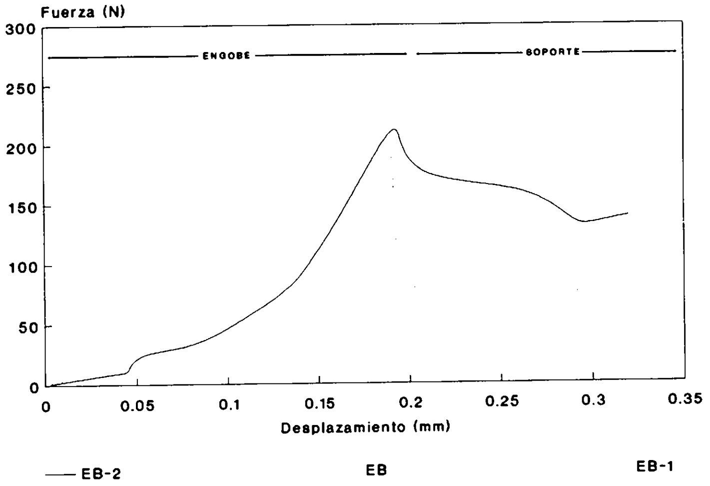

Figure 12. *Effect of bentonite content on EB engobe bonding*

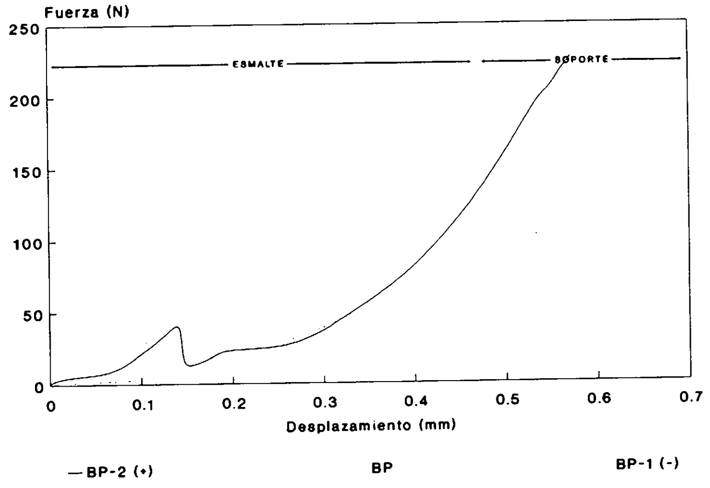

Figure 13. *Effect of binder content on BP glaze*

The effect caused by varying the amount of binder in the glazes was studied with white glazes BP, BP-1 and BP-2. Their behaviour in the bond test is depicted in Figure 13. When the amount of binder (BP-1) decreases, the second peak, close to the interface with the engobe, is associated with smaller force values, which indicates a lesser bonding of the glaze-engobe interface. However, on increasing the amount of binder (BP-2), the second peak does not appear, instead there is a gradual rise in force, showing greater bonding of the glaze to the engobe.

5.3.2 Effect of the amount of binder. Pieces with a double layer

Figure 14 shows the behaviour of pieces in which white glaze was applied to engobes containing varying amounts of CMC (BP white glaze and engobes EC, EC-1 and EC-2). In the case involving an increase in binder content, the peak value corresponding to the engobe area is only slightly higher than the peak value corresponding to the normal amount of CMC, and the engobe with less CMC exhibits a slightly lower peak. On comparing the data plotted in Figure 11, where only an engobe layer was involved, the behaviour is observed to be the same as with the superimposed glaze and engobe layers.

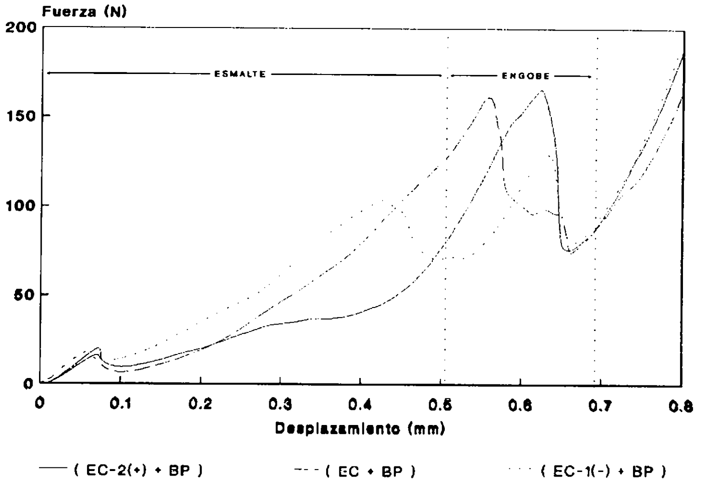

Figure 14. *Bonding between the white glaze and engobes with varying organic binder content*

In the glazes, two fractures arise in the layer in the case of white glaze BP applied to engobe EC-1: the first fracture, which is the same in the other studied cases (close to 0.10 mm) and a second fracture (approaching 0.40 mm), indicating that the bond between glaze and engobe is weaker than in the two foregoing cases, between which no significant differences were detected.

In those cases in which the amount of bentonite was varied in the engobe, with a subsequent application of white glaze (BP white glaze and engobes EB, EB-1, and EB-2), it was observed (Figure 15) that the white glaze bond hardly changed, keeping the same force values for the three engobes. In the area corresponding to the engobe, practically no variation can be observed with bentonite decrease, but on raising the bentonite content, there is an increase in the peak associated with the engobe-body interface, which in the other two cases is shifted towards the glaze-engobe interface, probably owing to the engobe layer being drawn along when the glaze layer fractures.

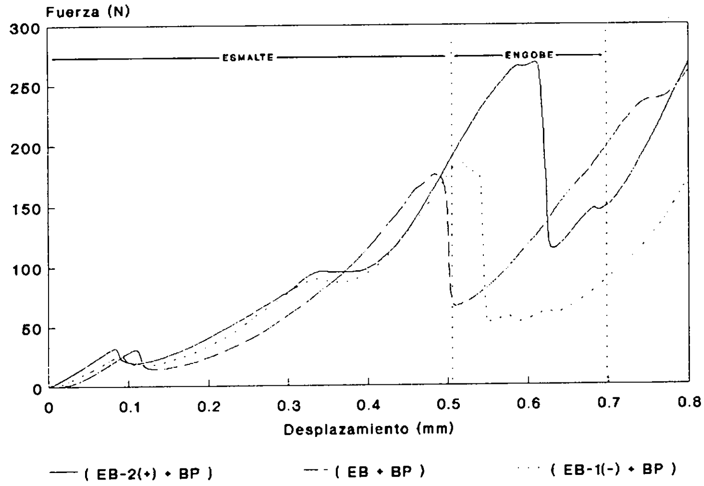

Figure 15. *Bonding between the white glaze and engobes with varying bentonite contents*

On modifying the amount of binder added to the white glaze (white glazes BP-1 and BP-2), which was applied to engobe EB, it became clear that with a decrease in CMC (BP-1), a loss of bonding occurs in the interface area as shown in Figure 16. This area exhibits two peaks in the curve associated with the BP-1 glaze layer, indicating greater brittleness. However, with a greater amount of CMC (BP-2), only one peak is found (at the glaze-engobe interface), with a higher force value.

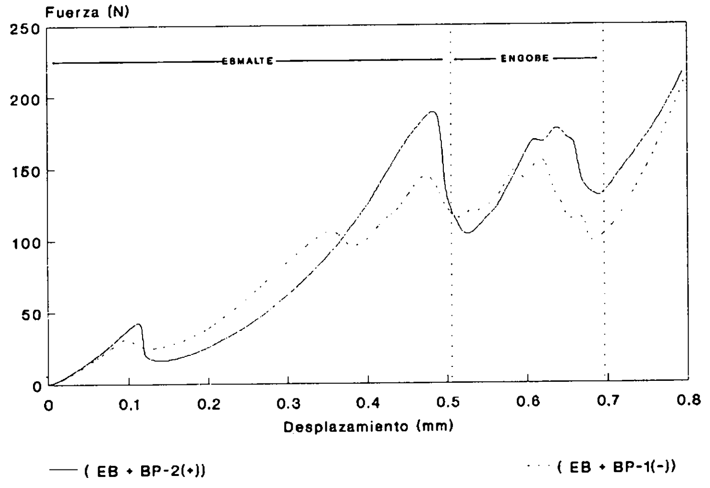

Figure 16. *Bonding of white glazes BP-1 and BP-2 with differing binder contents to engobe EB*

The effect is even more striking, when the decrease in CMC is marked, as is the case with glaze BP-3. Thus, Figure 17 shows that this layer presents very little resistance to deformation, with low force values being detected compared to the glaze with the normal CMC amount.

5.3.3 Effect of particle-size distribution

The two particle-size distributions tested in the glaze (white glazes BP-4 and BP-5), exhibited similar behaviour (Figure 18). However, the white glaze with the lower reject (BP-4) peaked in the area between 0.3 and 0.4 mm, which means fracture. This might have been caused by worse packing of the particles forming the layer, as it contained a larger amount of fines.

On applying these glazes to engobe EB (Figure 19), the behaviour exhibited resembles what was found on applying them to the body, as has been the case with the rest of the conducted tests.

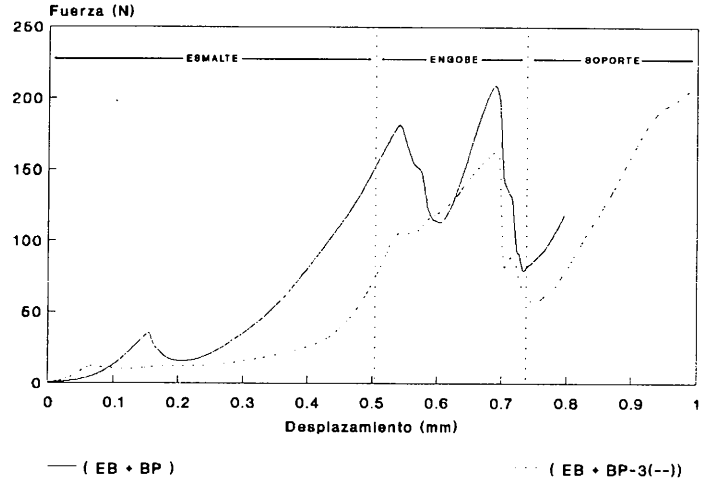

Figure 17. *Bonding of white glazes BP and BP-3 with differing binder contents to engobe EB*

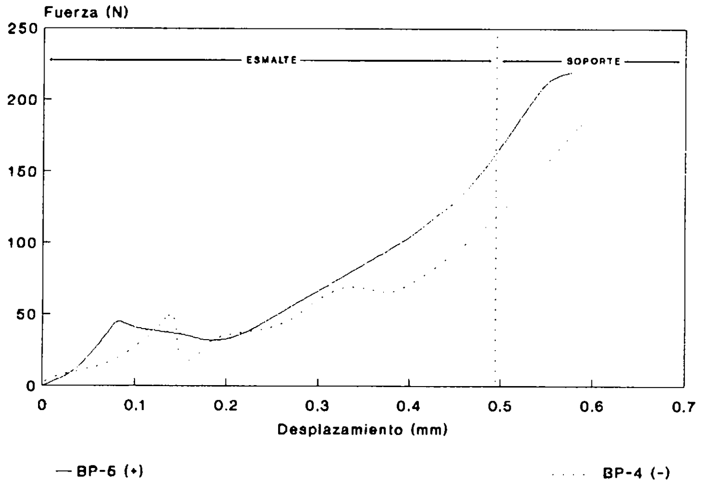

Figure 18. *Effect of particle-size distribution on the white glaze bond*

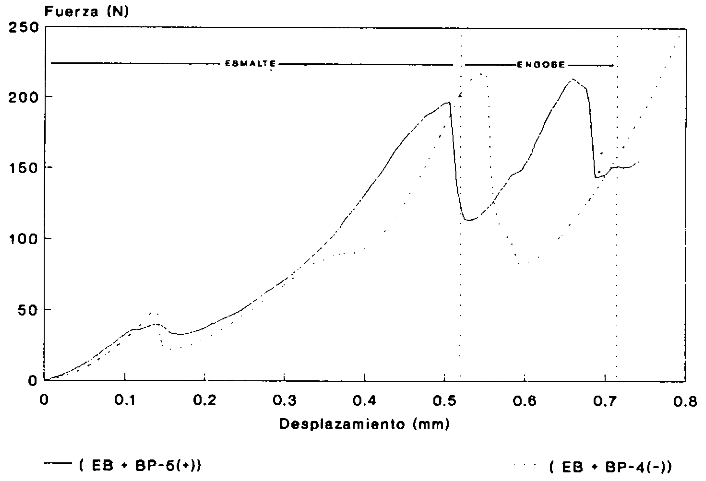

Figure 19. *Effect of particle-size distribution on white glaze bonding to the EB engobe*

5.3.4 Effect of varying the applied amount of glaze

Figure 20 plots the behaviour of bond strength on applying different amounts of BP white glaze to the EB engobe. These amounts were : 875, 1125 and 1375 g/m2, measured by the usual method of difference in weight of a piece before and after glaze application. The fracture peaks corresponding to the glaze layer do not exhibit significant differences, so that this variable does not affect the value of the recorded force.

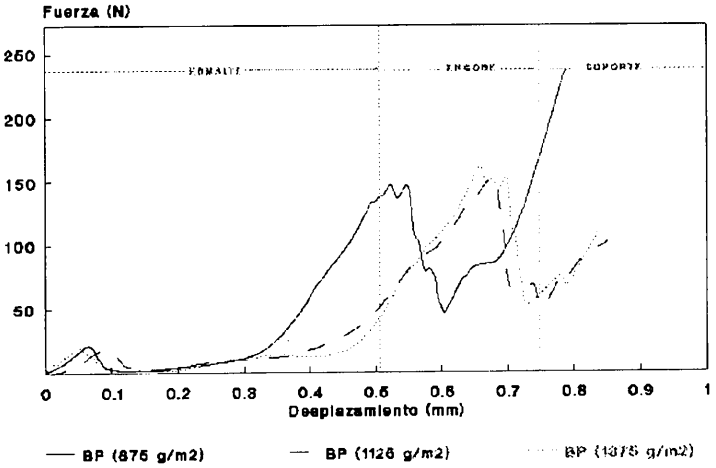

Figure 20. *Glaze BP and engobe EB bond with varying amounts of applied glaze*

5.3.5 Effect of varying body compaction

The variations in compaction were as follows: 1.90 , 2.03 and 2.11 g/cm3 respectively. Two peaks appear in the curve corresponding to the least compact body (Figure 21). This was due to fracturing of the engobe layer and of the body itself, which materialized almost simultaneously with these very low compaction values (1.90 g/cm^3). This makes it impossible to correctly assess bonding, but within the range of variation studied, the differences in compaction do not appear to affect the bonding of the tested materials.

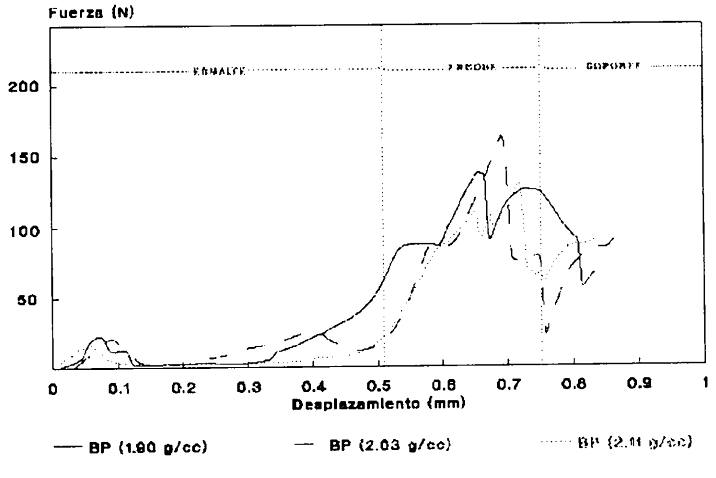

Figure 21. *Bonding of glaze BP and engobe EB with differently compacted bodies*

5.3.6 Effect of varying the CMC characteristics

Figure 22 plots the curve obtained with the values recorded of the force required to penetrate a glaze layer (BP-6), consisting of glaze that had been milled with CMC having a viscosity of 35-50 cp. CMC viscosity in the BP white glaze was 1000 cp. The same amount of CMC was used in both glazes. The graph shows that the behaviour is similar, without any differences in the force values being observed as a result of this variable.

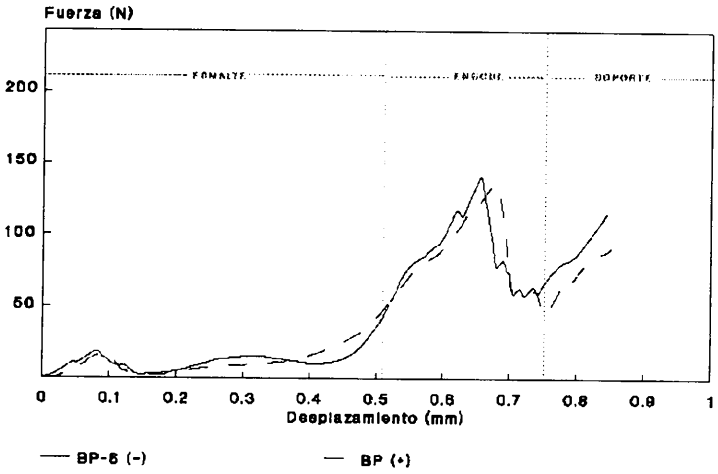

Figure 22. *Bonding of glazes BP and BP-6 (with CMC of differing viscosities) and engobe EB*

6. CONCLUSIONS

The following may be inferred from the results obtained:

- The method used has proved sufficiently valid to allow the differences in bonding exhibited by the studied materials to be established.
- The engobe containing bentonite showed greater bonding than the engobe with an organic binder.
- The engobes showed greater bonding than the glazes.
- No appreciable effect was found in the case of the materials used, that might be related to "ageing" of the suspensions.
- The behaviour of the layers obtained is similar when there is only a single layer, or when there are two superimposed layers.
- The relationship between the variation in binder content of the glazes and their bond strength was shown. It was observed that the organic binder had little impact on the engobe but an appreciable effect on the glaze, while the engobe containing bentonite proved to have greater bond strength, and was more sensitive to variation of this component.
- Modifying particle-size distribution had little effect on the characteristics of the glaze layer.
- The variation in the glaze amounts applied to the piece did not entail any changes in bond characteristics.

- Modifying the body compaction values did not give rise to any observable changes in the bonding of the engobe and glaze layers, in the studied variation range.
- Different kinds of organic binders (CMC of differing viscosities), did not significantly alter glaze bond characteristics.

7. REFERENCES

[1] HOUWINK, R. y SALOMON, G.. Adherencia y adhesivos. Traducido por C. Calvo. 2ªed. Bilbao : Ediciones Urmo. 1973. ISBN 84-314-0215-6

[2] ATKINSON, J.H. and BRANSBY P.L. The mechanics of soils. An introduction to critical state soil mechanics. London: McGraw-Hill. 1978. University series in civil engineering. ISBN 0-07-084077-6

[3] PARMELEE, C.W. Ceramic Glazes. 3ª ed. Boston :Cahners Books. 1973.

[4] ENRIQUE, J.E. AMOROS, J.L. y MONZO, M. Tecnología cerámica. Valencia : Instituto de Química Técnica (Tecnología Cerámica). 1985.

[5] AMOROS, J.L., BELTRAN, V., BLASCO, A., ENRIQUE, J.E., ESCARDINO, A., NEGRE, F. Defectos de fabricación de pavimentos y revestimientos cerámicos. Valencia : AICE-ITC. 1991. ISBN 84-604-0040-9

[6] REED, J. Introduction to the principles of ceramic processing. New York.: John Wiley & Sons. 1988. ISBN 0-471-84554-X.

[7] ZIMON, A. Adhesion of dust and powder. Translated by K.J. Robert. 2nd ed. New York : Consultants Bureau. 1982. NATO Conference series. Series VI, Materials Science; 3.ISBN 0-306-10962-X.