A STUDY OF HOW THE ENGOBE RESPONDS DURING THE GLAZING PROCESS.

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SUMMARY

The speed at which the engobe dries on the ceramic body whilst it is applied has a considerable effect upon the exterior characteristics and the appearance of the finished product.

Here, a study has been made of how the relationship between plastic materials and degreasants, the nature of the clay, the granulometric distribution of the engobe and the rheological state of the engobe slip all affect the time needed for the engobe to reach the required degree of wetness.

The results obtained have made possible a procedure whereby these characteristics can be controlled.

1.- INTRODUCTION.

When, as a result of one of the application processes, an engobe suspension comes into contact with a porous body (fired or unfired), water passes from the ceramic slip to the wall tile, due to the capillary suction effect created by the pores of the piece.

As the ceramic slip loses water, it starts to harden and a layer of porous material forms, through which the rest of the water in the slip flows, until it has been completely absorbed. The characteristics of this layer which forms considerably affect not only the time needed for the applied slip to harden, but also the time following applications will take to dry.

1.1.- Permeability of the engobe layer. Evaluation of the same by means o experiments using traditional, casting techniques.

For the traditional casting process (1), in which it is assumed that the permeability to water of the gypsum cement mold is considerably greater than the permeability to water of the hardened layer (Kp), the relationship between the speed of casting (L /t) and Kp can be expressed as follows:

$$\frac{L^2}{t} = \frac{2P\,Kp}{Ln} \qquad [1]$$

in which:

L = thickness of hardened layer.
t = casting time.
P = capillary suction pressure of cast.
n = viscosity of liquid.

$$n = \frac{1\text{-}s\text{-}}{s} \qquad [2]$$

s = volumetric fraction of solids in the suspension.
= porosity of the layer formed.

In the light of equation [1], if the values of L are plotted against time (t), these values having been obtained in an experiment using traditional casting techniques, a straight line should be obtained , the angle of which is governed by the viscosity of the liquid (), generally water, by the solid content of the slip (s), by its porosity () and by the permeability of the engobe (Kp).

As a consequence, when different engobes are tested using the same type of gypsum cement mold (P =cte), whilst the casting temperature is kept constant, different values will be obtained for the speed at which the wall forms (L /t), from which, applying equation [1], the permeability (Kp) of the engobe layer which has formed can be calculated.

2.- PURPOSE AND SCOPE OF THIS INVESTIGATION.

In addition to the rheological characteristics of the suspension, the speed at which the engobe wall forms (L /t), and the permeability of the layer formed (Kp) greatly condition the behaviour of the engobe during the glazing process. For this reason it was considered to be worthwhile to have more information on this subject, and thus this study was programmed to be carried out in accordance with the following plans:

i) The setting up of experimental procedures in order to determine the speed at which the walls of different engobes form, using the same type of gypsum cement mold, and to analyse the different raw materials, suspensions and engobes.

ii) The planning and execution of a series of experiments in order to determine what influence the type and quantity of the clay minerals have upon the rheological characteristics of the suspension, the speed at which the layer forms and the permeability of the engobe.

iii) The completion of a series of experiments with an industrial engobe, in which preparation conditions were modified, with a view to determine what effect the degree to which the components are ground, the solid content and the rheological state of the suspension all have upon the speed at which the wall forms and upon the permeability of the engobe.

3.- MATERIALS AND EXPERIMENTAL PROCEDURE.

3.1.- Materials.

The compositions of the different engobes were prepared from a frit (F) and from different raw materials.

In table I the chemical analyses of the aforementioned materials are presented in detail and in table II their corresponding granulometric distribution and their specific surfaces (Sp) are shown.

	Arcilla 1	Arcilla 2	Arcilla 3	Arcilla 4	Feld.sod.	Zircon	Arcilla 5	Frita
SiO_2	64.00	49.00	47.60	71.66	60.20	32.80	48.00	63.00
Al_2O_3	24.00	34.00	36.10	15.65	23.30	0.01	37.00	7.61
Fe_2O_3	1.10	1.70	1.30	0.84	0.08	0.07	0.75	0.37
TiO_2	1.20	1.00	1.30	0.14	--	0.15	0.02	--
MgO	0.40	0.30	0.10	1.79	--	--	0.30	0.68
CaO	0.30	0.30	0.20	1.02	0.30	--	0.06	4.34
K_2O	2.40	1.20	0.40	1.98	5.10	0.01	1.90	3.36
Na_2O	0.40	0.20	0.10	1.49	10.60	0.01	0.10	2.71
ZrO_2	--	--	--	--	--	66.00	--	8.38
B_2O_3	--	--	--	--	--	--	--	8.48
PbO	--	--	--	--	--	--	--	0.33
ZnO	--	--	--	--	--	--	--	0.37
P.P.C.	7.00	12.00	12.90	6.21	0.40	--	12.10	--

TABLE I
Chemical analysis of the components used in the formulation of engobes.

Di (µ)	Arcilla 1	Arcilla 2	Arcilla 3	Arcilla 4	Desgras.	Feld. sod	Zircon	Arcilla 5
80	100	100	100	100	96	100	100	100
60	100	100	100	98	92	100	100	98
40	100	100	100	97	78	98	100	94
20	98	97	94	97	58	81	100	84
10	90	91	98	96	43	53	100	65
5	78	84	92	92	33	33	96	43
2	60	68	84	88	21	20	63	20
1	47	56	70	87	12	13	32	12
0.5	27	35	57	86	2	9	10	6
Sp (m^2/g)	23.26	36.65	23.50	43.71	0.50	1.63	12.2	13.16

TABLE II
Values of the specific surfaces and granolumetric distribution of the materials used in the formulation of engobes.

3.2.- Experimental procedure.

3.2.1.- Preparation of the engobes.

The raw materials were mixed in suitable proportions and equalized in a laboratory ball mill by a dry method. To determine the rheological conditions of the engobe suspension required to carry out the casting test, the deflocculation curve of each of the compositions was calculated by means of a torsion wire viscometer. Except in those experiments in which the aim was to determine the effect of the rheological conditions of the suspension upon the response of the engobe, all the suspensions were prepared under the conditions corresponding to the minimum deflocculation curve. The solid content used was 71% ; in the experiments aiming to determine the effect of this variable, suspensions of 73% and 75% were prepared. The rejection value at 40 obtained was approximately 1.5%, except in those experiments in which the casting time was deliberately altered in order to analyse the effect of this change.

3.2.2.- Determining the speed at which the wall forms.

The procedure consists of measuring the thickness of the engobe layer which forms on the gypsum cement mold while the latter sucks in the water from the suspension.

3.2.2.1.- Preparation and analysis of the gypsum cement mold.

In figure 1 details are found of the distribution according to size of the gypsum cement mold pores, and in table III the most important properties of the mold are shown.

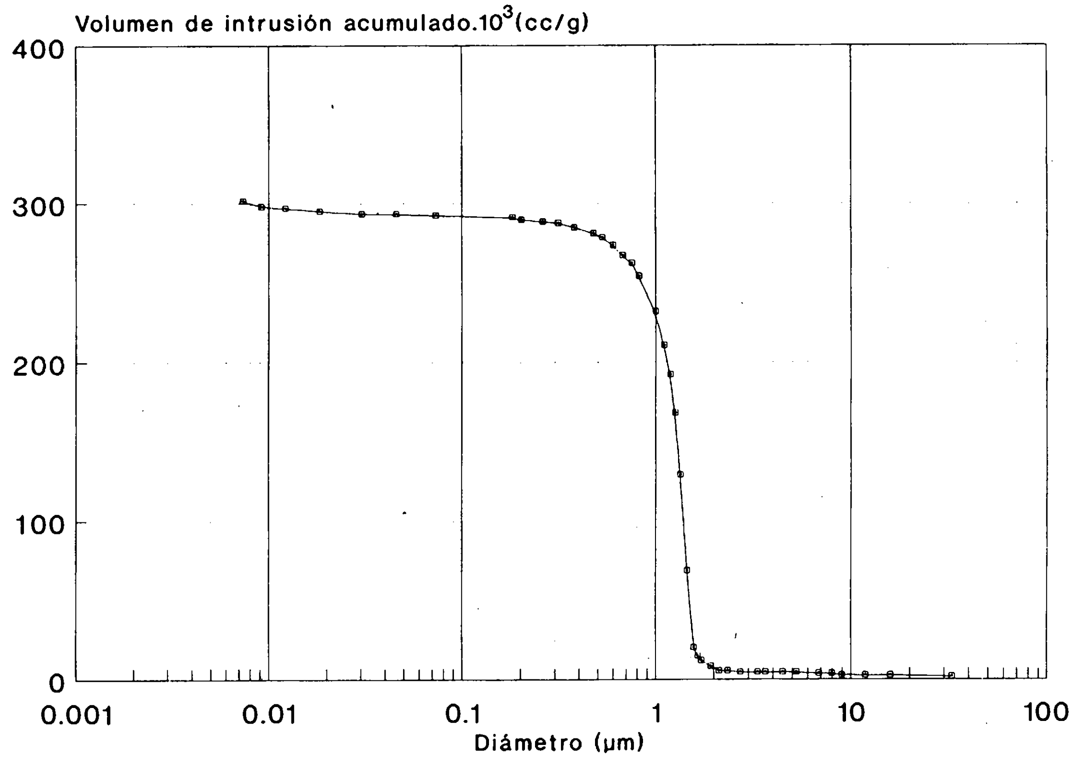

Figure 1.- Distribution according to size of the gypsum cement mold.

TABLE III
Properties of the gypsum cement mold.

Open porosity = 0.288
Apparent density = 1352 Kg/m3
Coefficient of suction = 0.18 Kg/m2 s1/2

Based on the values of table III, a value of 48.913 N/m has been calculated (2) to measure the capillary suction pressure (P) for this cast.

3.2.2.2.- Casting test.

The test cylinder of gypsum, fastened to a rod (figure 2), comes into contact with the engobe suspension for a certain period of time. When the desired period of time has elapsed, the test cylinder is removed, and the thickness of the layer and its porosity can be calculated from its humidity content.

4.-RESULTS AND CONSIDERATIONS.

4.1.- Influence of the engobe composition upon the rheological response of the suspension, upon the speed at which the wall forms (L /t) and upon the permeability of the layer which forms (Kp).

To investigate the above, different compositions were prepared, based on a formula widely used in the industry (C1), modifying the proportions of its plastic conponents (table IV).

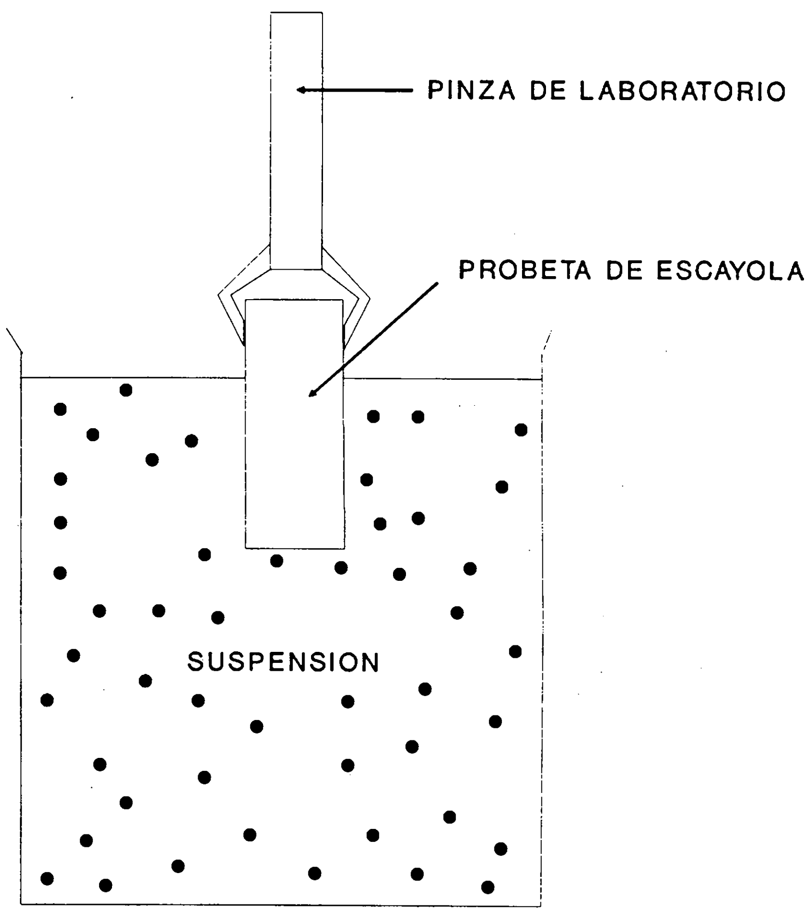

Figure 2.- Test to determine speed at which wall forms.

Componente / Composición	C_1	C_2	C_3	C_4	C_5	C_6	C_7
Arcilla 1	18	23.4	11.8	--	--	9	18.4
Arcilla 2	--	--	--	18	--	--	--
Arcilla 3	--	--	--	--	18	--	--
Arcilla 4	2	1.9	2.1	2	2	2	--
Arcilla 5	--	--	--	--	--	9	--
Silicato de Zirconio	10	9.3	10.8	10	10	10	10.2
Frita	25	23.4	26.9	25	25	25	25.5
Desgrasante	25	23.4	26.9	25	25	25	25.5
Feld. Sódico	20	18.7	21.5	20	20	20	20.4

TABLE IV
Laboratory-prepared engobe compositions

4.1.1.- Effect of the clay content.

On examination of the deflocculation curves (fig.3) corresponding to the compositions C1, C2, and C3, it can be deduced that, as the clay content increases, so too does the viscosity of the suspension and the quantity of deflocculant that must be added in order to attain the minimum viscosity also increases.

Figure 4 shows the squared value (L) of the thickness of the engobe layer forming against the value of time for the three compositions, operating under conditions of minimum viscosity. In table V details are found of the values of the speed at which the wall forms (L /t) obtained by lineal regression from the values L and t in figure 4. Also included in this table are the values of the porosity of the layer () and those of the permeability coefficient (Kp). The latter were calculated from the values of (L /t) of and from the characteristics of the suspension, applying equation (1).

TABLE V.- Influence of the clay content upon the characteristics of the engobe

Composition	clay (%)	e	$L^2/t\ 10^8$ (m^2/s)	Kp 10^{17} (m^2)
C_1	18	0.40	1.10	3.1
C_2	23.4	0.39	0.95	2.7
C_3	11.8	0.40	1.40	3.8

On examination of Figure 4 it can be seen that the results produce straight lines, in the case of each composition, as equation [1] predicts.

In addition, it can be noted that the speed at which the wall forms, together with the coefficient of the permeability of the engobe layer, decrease as the clay content increases, while the porosity () hardly changes.

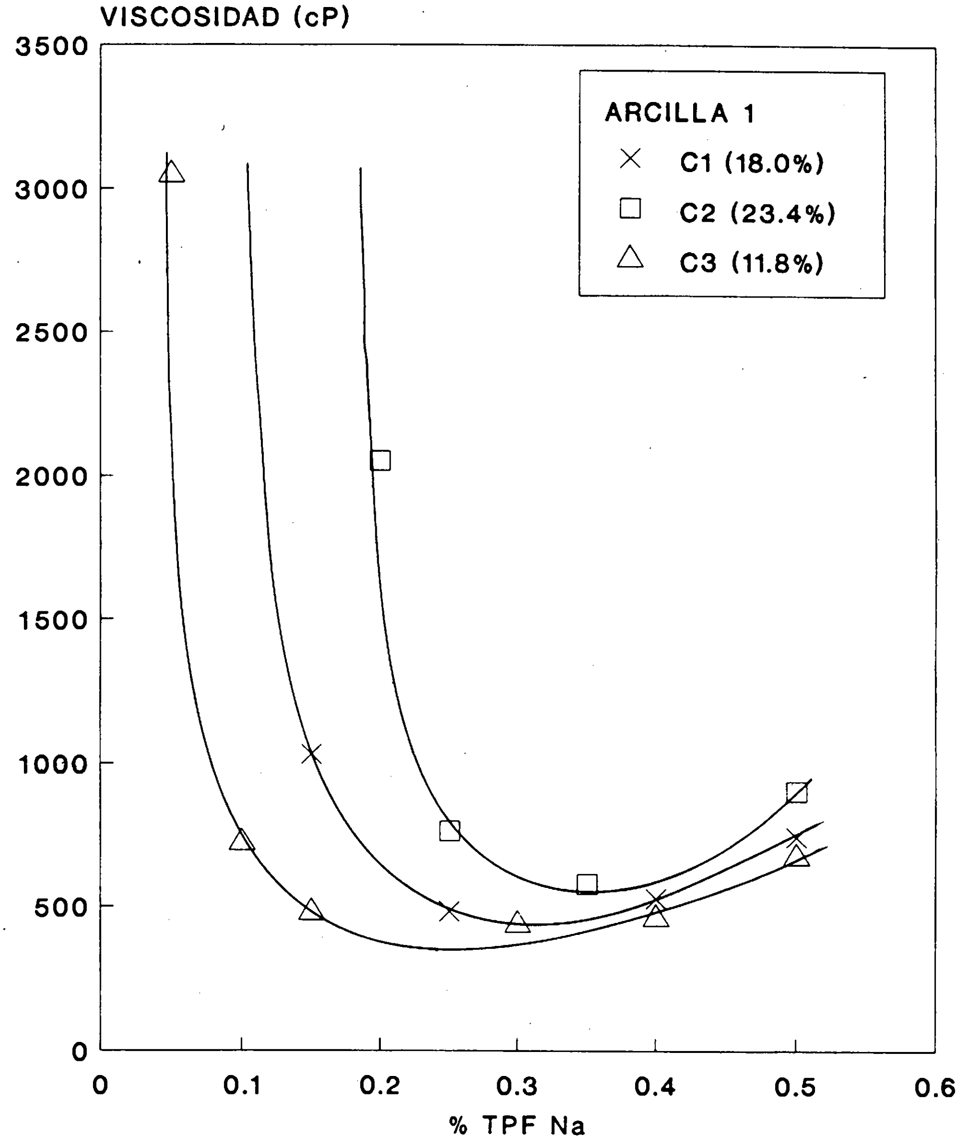

Figure 3.- Influence of the content of clay sample 1 upon the rheological characteristics of the engobe suspension.

4.1.2.- Importance of the nature of the plastic components.

When comparing the deflocculation curves (figure 5) corresponding to the compositions which have the same clay content (C1, C4 and C5), it can be seen that engobe C4, produced with a clay of greater specific surface, shows greater viscosity than the other two engobes and also needs a higher deflocculant content to reach the minimum degree of viscosity. The other two engobes produce curves which are very similar to each other. Nevertheless, because the clay sample 3 contains less organic material, the suspension of engobe C5 has less viscosity and requires a deflocculant content which is also lower (4).

On the other hand, when one compares the deflocculation curves corresponding to compositions C1 and C7, it can be seen that when clay sample 4 (of greater specific surface) is removed from the composition, the viscosity of the suspension is considerably reduced. However, a partial substitution of clay sample 1 with sample 5 (which has a lesser specific surface) only reduces the interval of deflocculation (curves C1 and C6).

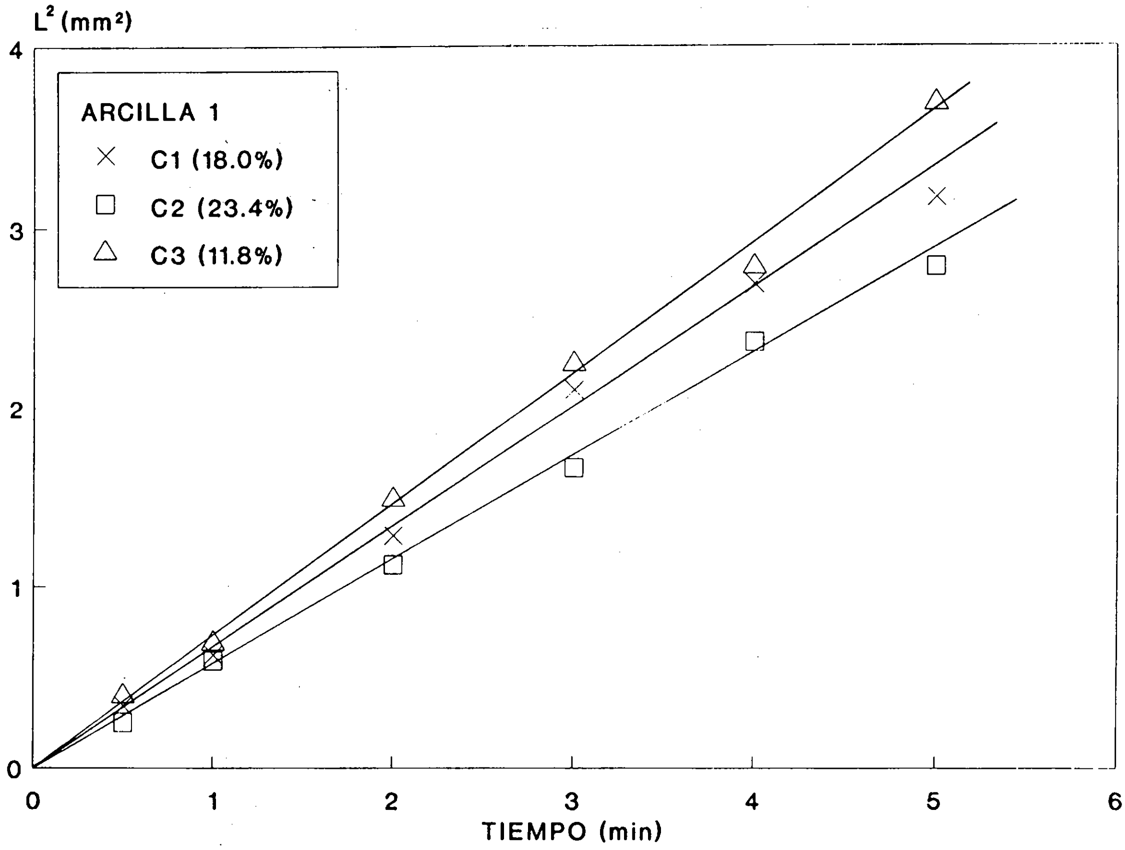

Figure 4.- Influence of the content of clay sample 1 on the speed at which the engobe wall forms.

Figure 6 shows the results obtained from the experiments to test the speed at which the wall forms and table VI sets out the values of the casting speed (L /t) and of the permeability (Kp) and porosity () of the layer, these values corresponding to compositions C1, C4, C5, C6 and C7.

TABLE VI
Influence of the mineral nature of the clay upon the characteristics of the engobe.

Composition	$L^2/t10^8$ (m^2/s)	ε	Kp 10^{17} (m^2)
C1	0.40	1.10	3.1
C4	0.40	0.85	2.4
C5	0.39	1.15	3.3
C6	0.40	1.45	4.1
C7	0.39	1.15	3.2

On examination of these results the following can be concluded:

i) The porosity of the engobe layer which forms does not alter appreciably when the composition is changed.

ii) If clay sample 3 (which has a much greater specific surface) is substituted for sample 1, the casting speed (L /t) and the permeability of the engobe layer (Kp) are considerably reduced.

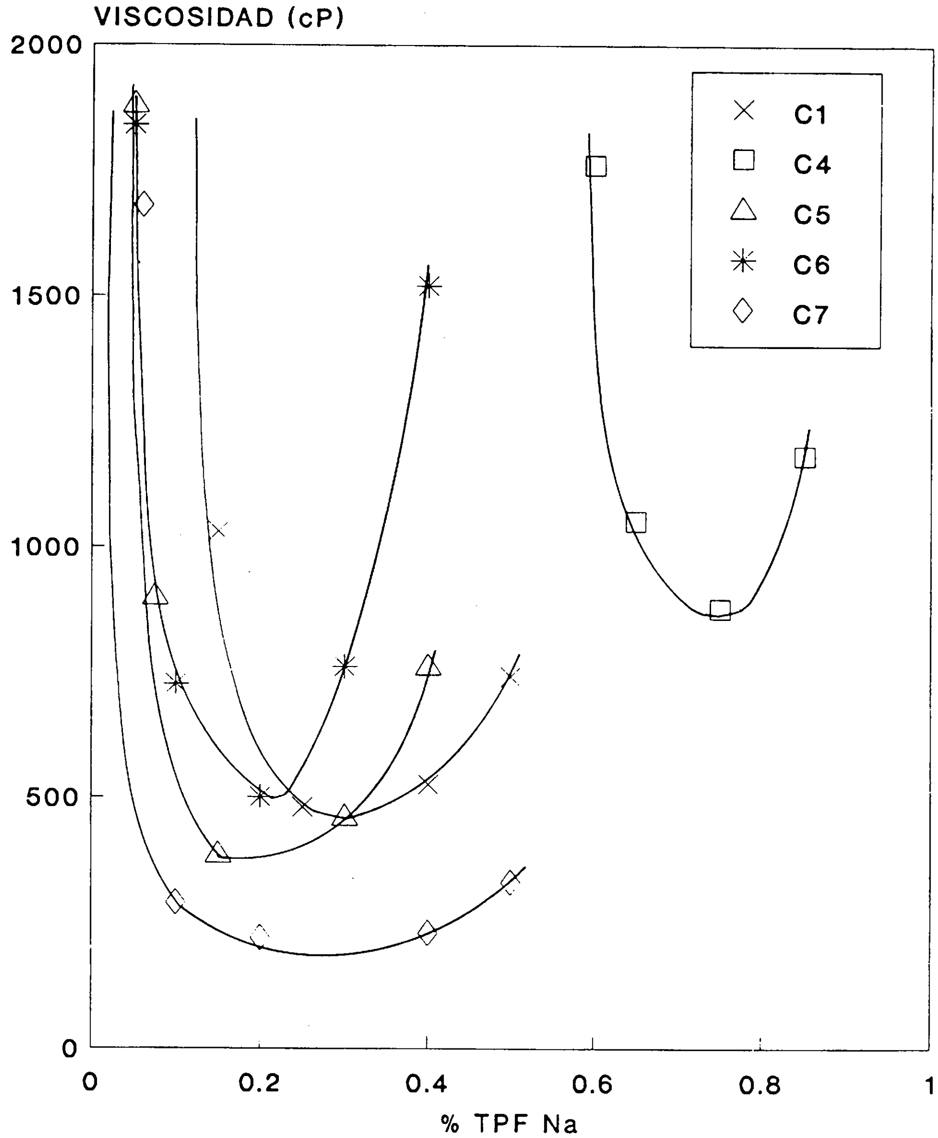

Figure 5.- Influence of the mineral nature of the clay upon the rheological response of the engobe suspension.

iii) The partial substitution of clay sample 5 (which has a lesser specific surface) for sample 1 considerably increases the permeability of the engobe layer (Kp) and as a consequence, the speed at which the wall forms (L /t).

iv) Neither by eliminating clay sample 4 from composition C1, nor by substituting sample 3 for sample 1 (both of which have very similar specific surfaces) are the permeability (Kp) of the engobe layer and the casting speed (L /t) significantly changed.

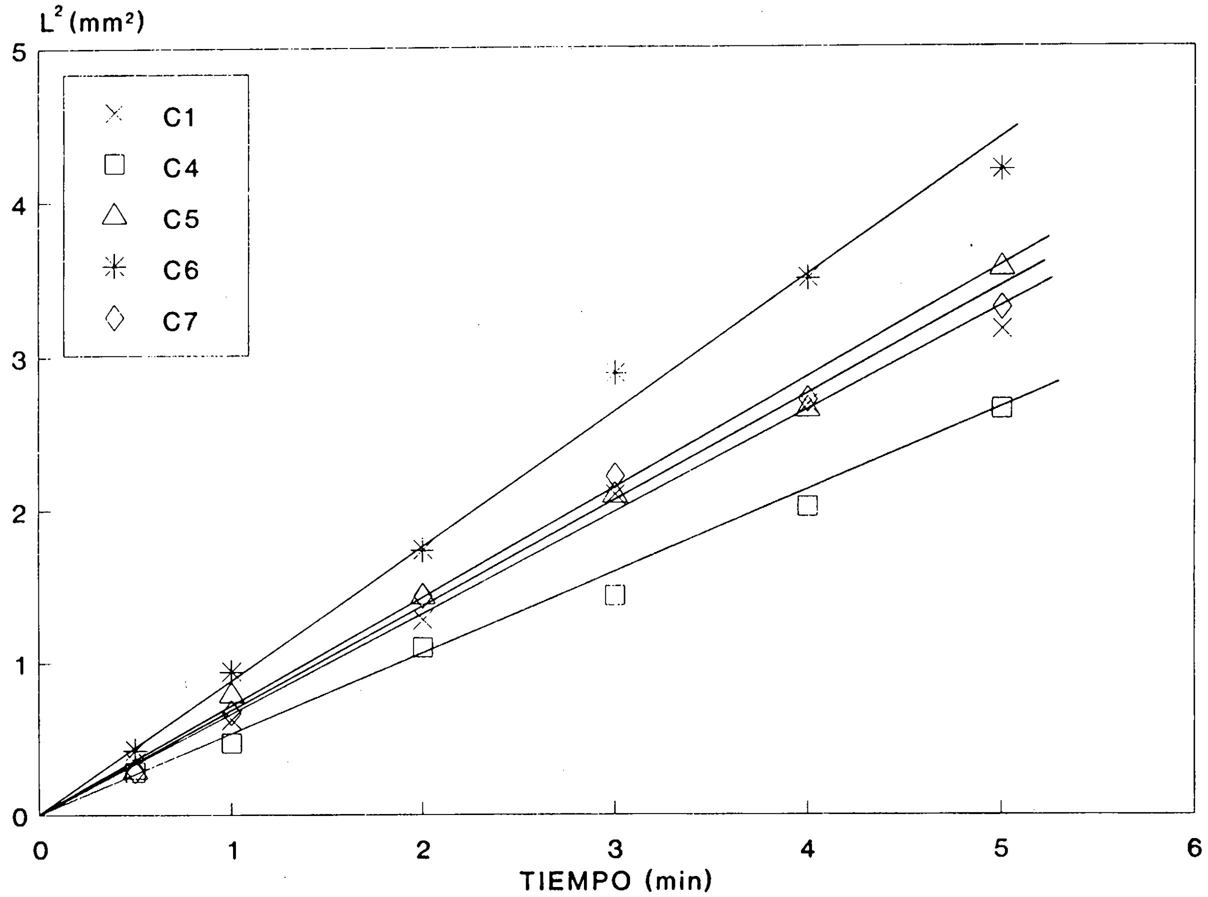

Figure 6.- Influence of the mineral nature of th clay on the speed at which the engobe wall forms.

4.1.3.- Relationship between the coefficient of the permeability of the engobe layer (Kp) and its specific surface (Sp).

In the previous sections it has been observed that, keeping the solid content of the suspension (s) constant and operating under conditions of minimum viscosity, if the nature and/or proportion of plastic materials in the composition are modified, the porosity of the engobe layer which forms is not affected, and for this reason, in accordance with equation [1], the casting speed (L /t), for these compositions, bears direct relation to the permeability coefficient of the layer formed (Kp).

On the other hand, it has been seen that, when the specific surface of the engobe is increased, by using a higher clay content and/or modifying the nature of the plastic component, the permeabilty coefficient of the engobe layer (Kp) decreases. These results are consistent with those predicted by theoretical models referring to the permeability of a porous bed (5) (6). In fact, with the increase in the specific surface of the particles in a suspension, the size of the capillaries of the porous bed decreases and they probably become more tortuous, which brings about an increase in the resistance of these tightly-packed particles to the flow of fluids through them.

In an attempt to establish a quantitative relationship between the permeability of the layer formed (Kp) and the specific surface of the engobe (Sp), applying the values of Kp in table V and VI and those of Sp calculated from the values of the different raw materials, various ways of setting out these values have been tried.

Pag.18Of these, the most suitable is shown in figure 7, where Kp values are plotted against Sp values on a double logarithmic scale. It can be seen that the points on the graph, although disperse, can be represented by the equation:

$$Kp = 2.13\,10 \quad Sp \qquad [3]$$

These results reveal that, in the case of those compositions in which the porosity of the porous bed barely changes, the permeability of the engobe layer (Kp) and thus the speed at which the engobe wall forms (L /t) are inversely related to the specific surface of the suspension (Sp).

4.2.- Influence of the operational conditions upon the rheological response of the suspension, upon the speed at which the wall forms (L /t) and upon the permeability of the layer formed (Kp).

In investigating the above, we used the formulation C1, and appropriate modifications were made to the viscosity, the solid content and the extent to which the suspension was ground.

4.2.1.- Effect of variations in the grinding.

To study the effect of this operational variable, three suspensions of the engobe C1 were used with rejection values at 40 of 0.2, 1.5 and 6%, the length of time spent in grinding being appropriately modified.

The deflocculation curves corresponding to these suspensions are very similar, as can be seen in figure 8. This leads us to confirm that the size and percentage of the colloidal particles, these being the particles which to a great extent determine the rheological response of the suspension, do not change when the grinding time is modified (7).

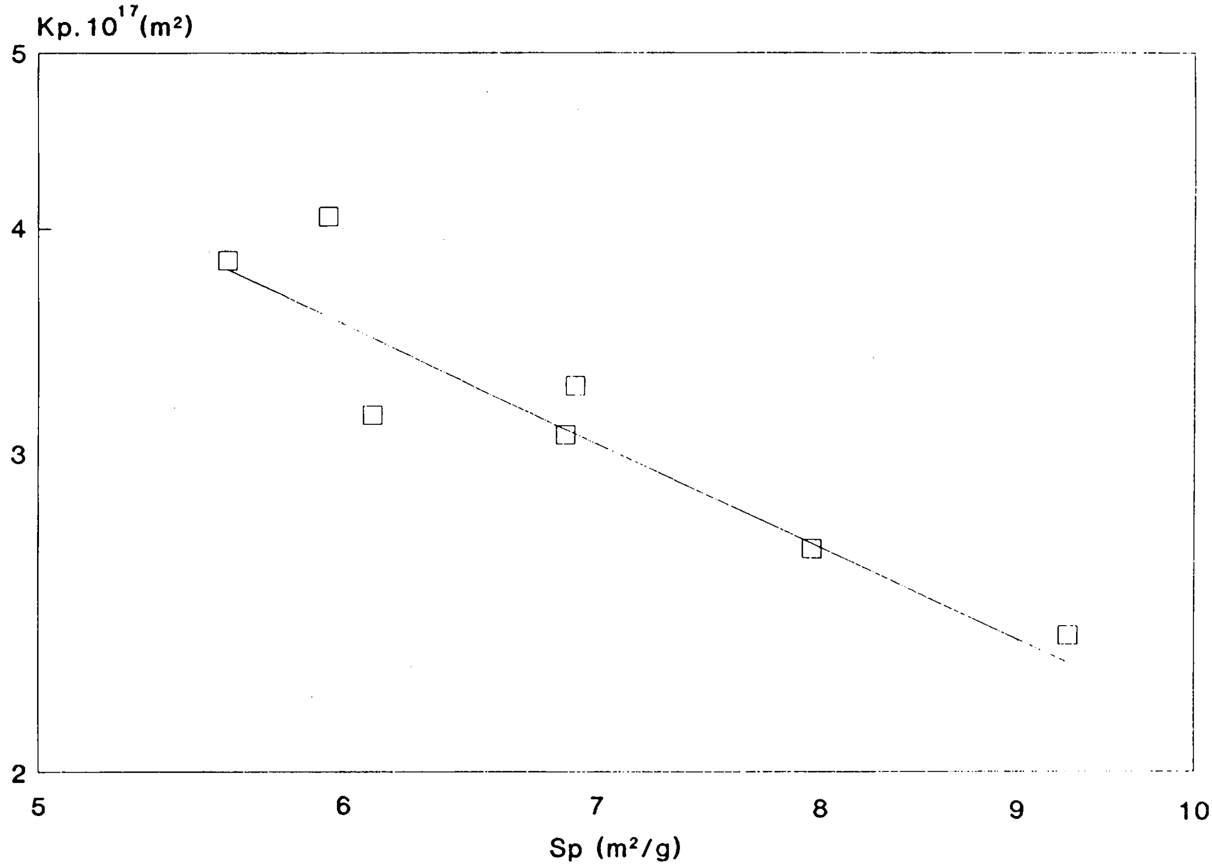

FIGURE 7.- Relationship between the coefficient of the permeability of the engobe layer (Kp) and its specific surface (Sp).

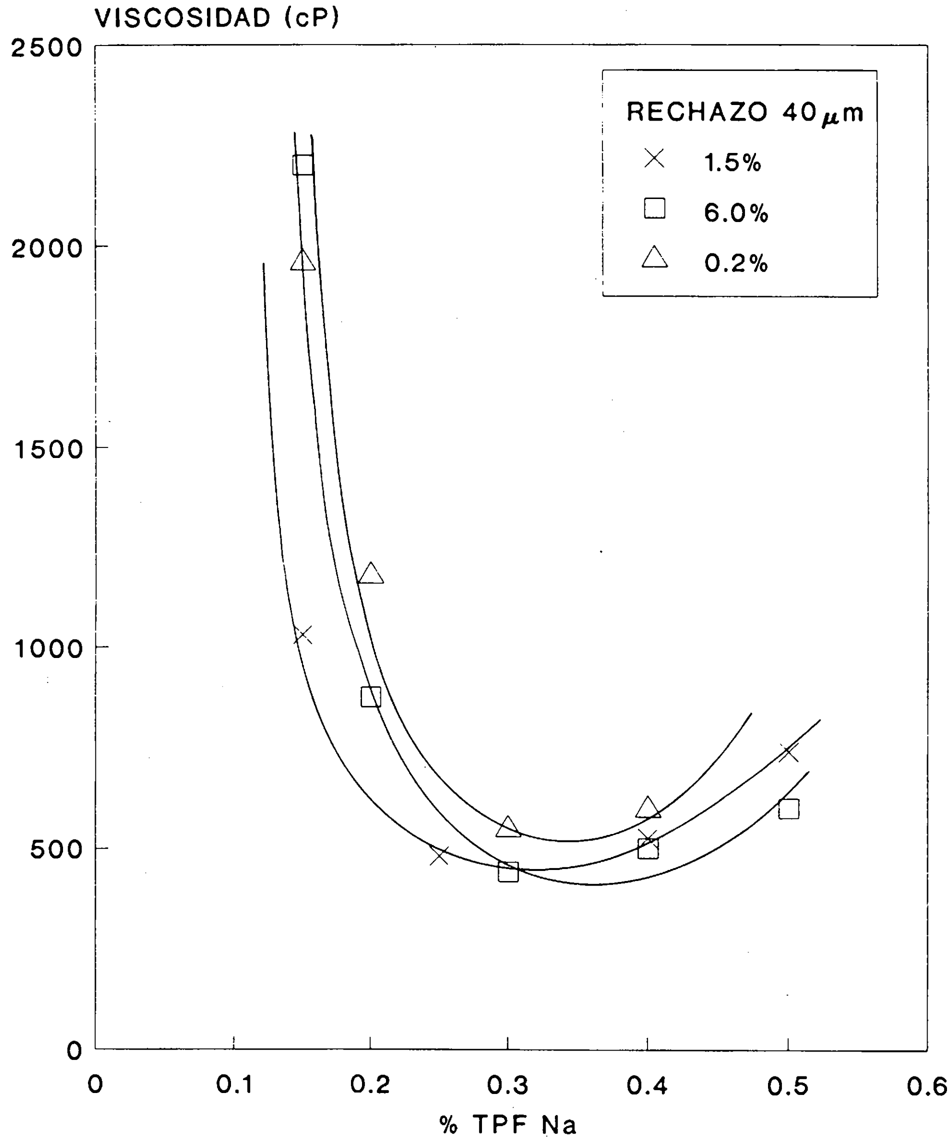

Figure 8.- Influence of the degree to which the engobe is ground upon its rheological response.

Figure 9 shows the results obtained from the experiments on the speed at which the wall forms, and table VII sets out the values of the casting speed (L /t), of the permeability (Kp) and porosity () of the layer and of the parameter n (equation [2]), for these three suspensions.

TABLE VII
Influence of the extent of grinding upon the characteristics of engobe C1.

Rejection at 40 μm (%)	ε	$L^2/t\ 10^8$ (m^2/s)	$Kp.10^{17}$ (m^2)	n
0.2	0.41	1.10	2.9	0.25
1.5	0.41	1.10	3.1	0.28
6.0	0.37	0.60	2.0	0.34

On examination of these results it can be seen that a reject increase, caused by insufficient grinding, results in a marked decrease in the engobe's porosity (), its permeability (Kp) and in the speed at which the walls are formed (L /t). In fact, for this kind of composition, an increase in the size and percentage of the degreasants, without modifying the fraction of colloidal particles, improves the tight packing of the particles of the porous bed (8) and as a consequence their permeability (Kp) decreases (9) and parameter n increases (equation [2]). The simultaneous increase in the value of these factors (Kp and n) results in a noticeable decrease in the casting speed (L /t), in accordance with equation [1].

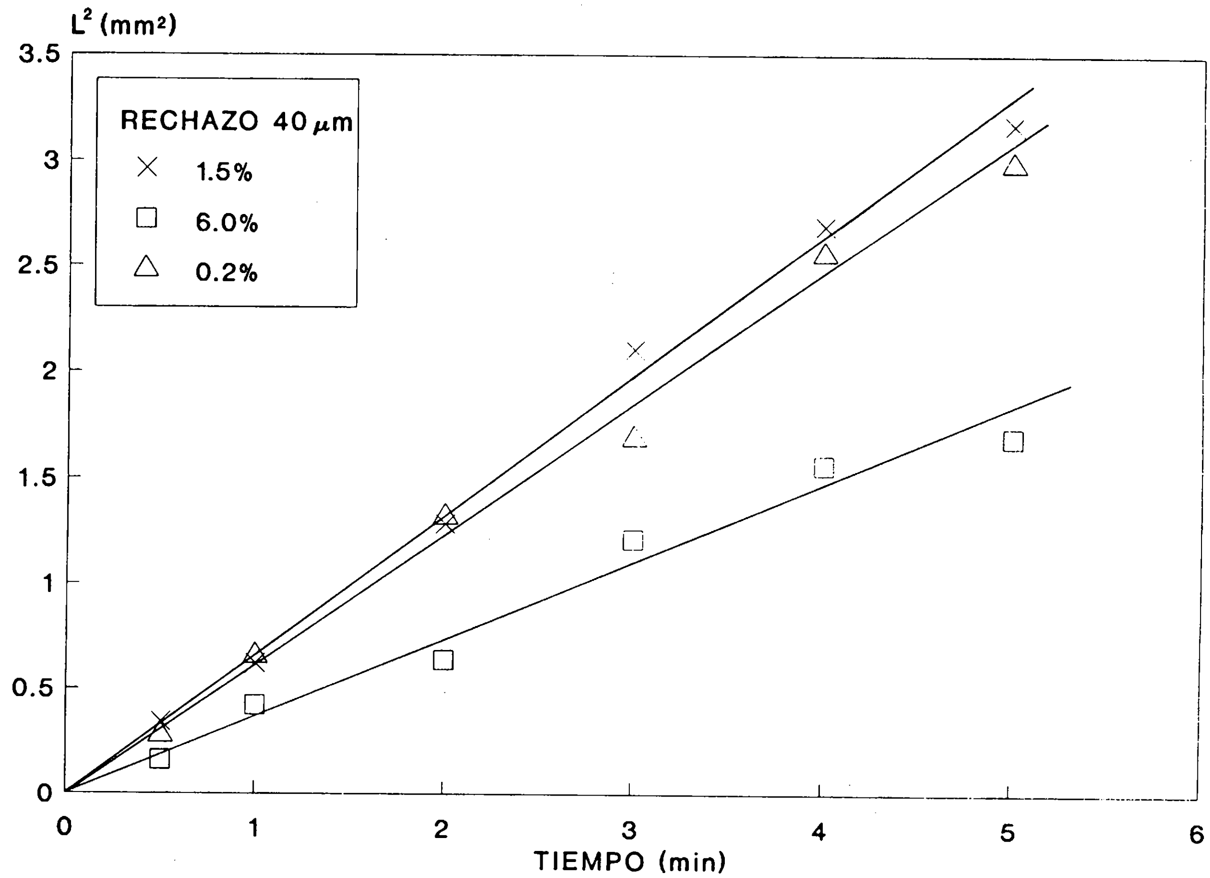

Figure 9.- Influence of the extent to which engobe C1 is ground upon the speed at which the wall forms.

4.2.2.- Effect of the state of deflocculation of the suspension.

In order to determine the effect of the state of deflocculation of the suspension upon the speed at which the engobe wall forms and upon the properties of the layer formed (Kp and), beginning with composition C1, three suspensions of very different viscosity were prepared, using 3 mixtures containing sodium tripoliphosphate (figure 10).

The results obtained from the experiments investigating the speed at which the wall forms are shown in figure 11 and are set out in detail in table VIII.

It can be seen from these results that the flocculate (F) and overdeflocculate (S) suspensions, since they keep the particles closely massed together, lead to the formation of more porous and permeable layers than the deflocculate suspension C1.

TABLE VIII

Influence of the state of deflocculation of the suspension upon the characteristics of engobe C1.

Suspension	ε	$L^2/t\ 10^8$ (m^2/s)	Kp 10^{17} (m^2)	n
D	0.40	1.10	3.1	0.28
F	0.44	1.80	3.4	0.19
S	0.43	1.70	3.5	0.21

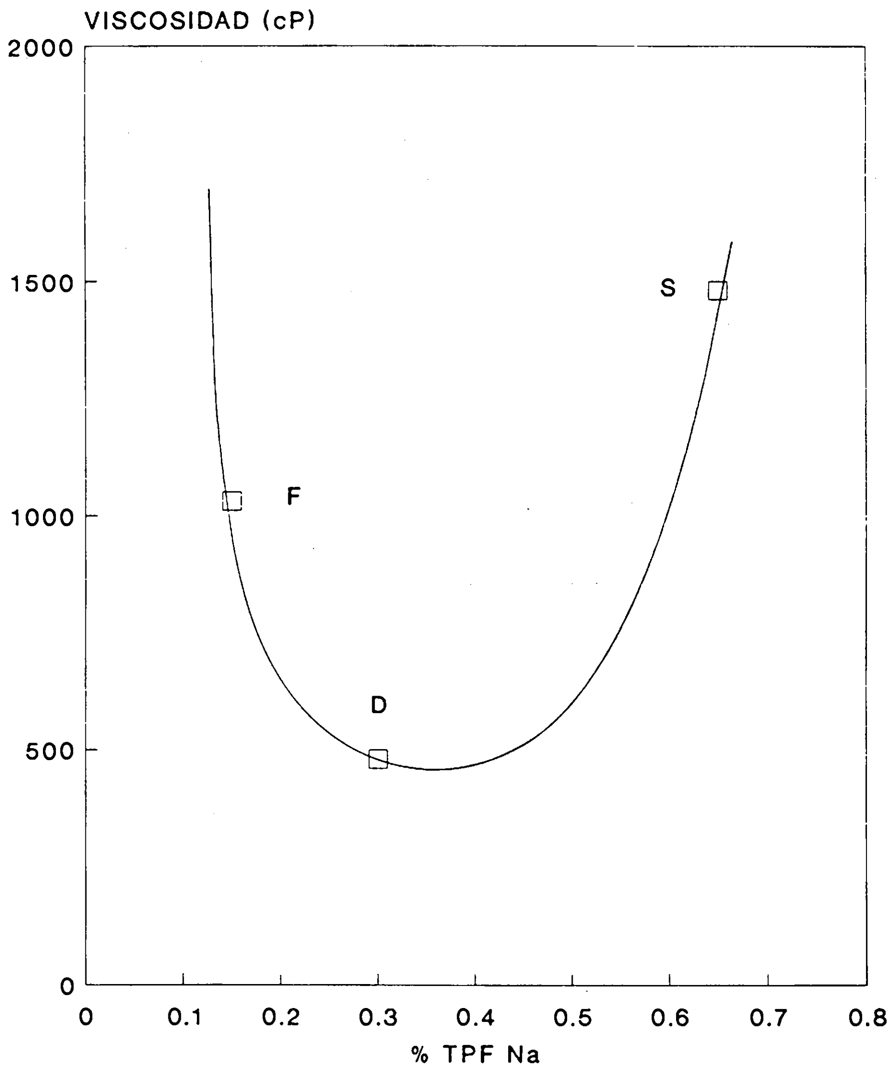

Figure 10.- Rheological conditions used to determine the influence of the state of deflocculation of the suspension upon the speed at which the wall forms.

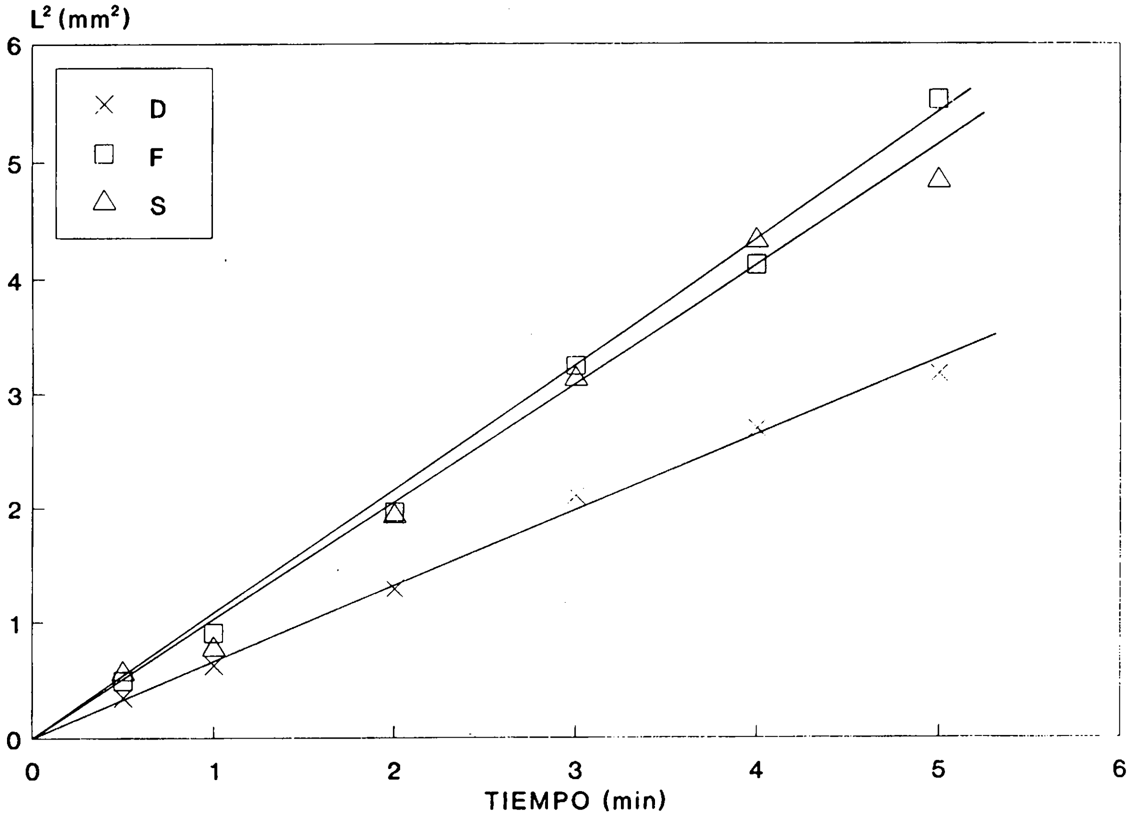

Figure 11.- Influence of the state of deflocculation of the engobe C1 suspension upon the speed at which the wall forms.

The increase in permeability (Kp) and the diminishing of parameter n, the latter being due to the increase in porosity (equation [2]), in both cases the result of the agglomeration of particles in the suspension, lead to a considerable increase in the casting speed (L /t).

4.2.3.- Effect of the solid content of the suspension.

Figure 12 shows the deflocculation curves corresponding to the suspensions of compositon C1, prepared with a 71, 73, and 75% solid content. It can be seen that there is an increase in viscosity and a decrease in the deflocculation interval, proportionate to the increase in the solid content of the suspension (s).

Figure 13 and table IX show in detail the results of the tests on the speed at which the wall forms.

TABLE IX

Influence of the solid content of the suspension upon the characteristics of engobe C1.

Solid content	ε	$L^2/t\ 10^8$ (m^2/s)	Kp 10^{17} (m^2)	n
71	0.40	1.10	3.1	0.28
73	0.40	1.40	3.1	0.22
75	0.39	1.65	2.9	0.17

On examination of these results, it can be seen that by increasing the solid content of the suspension (s), the speed at which the wall forms increases (L /t),

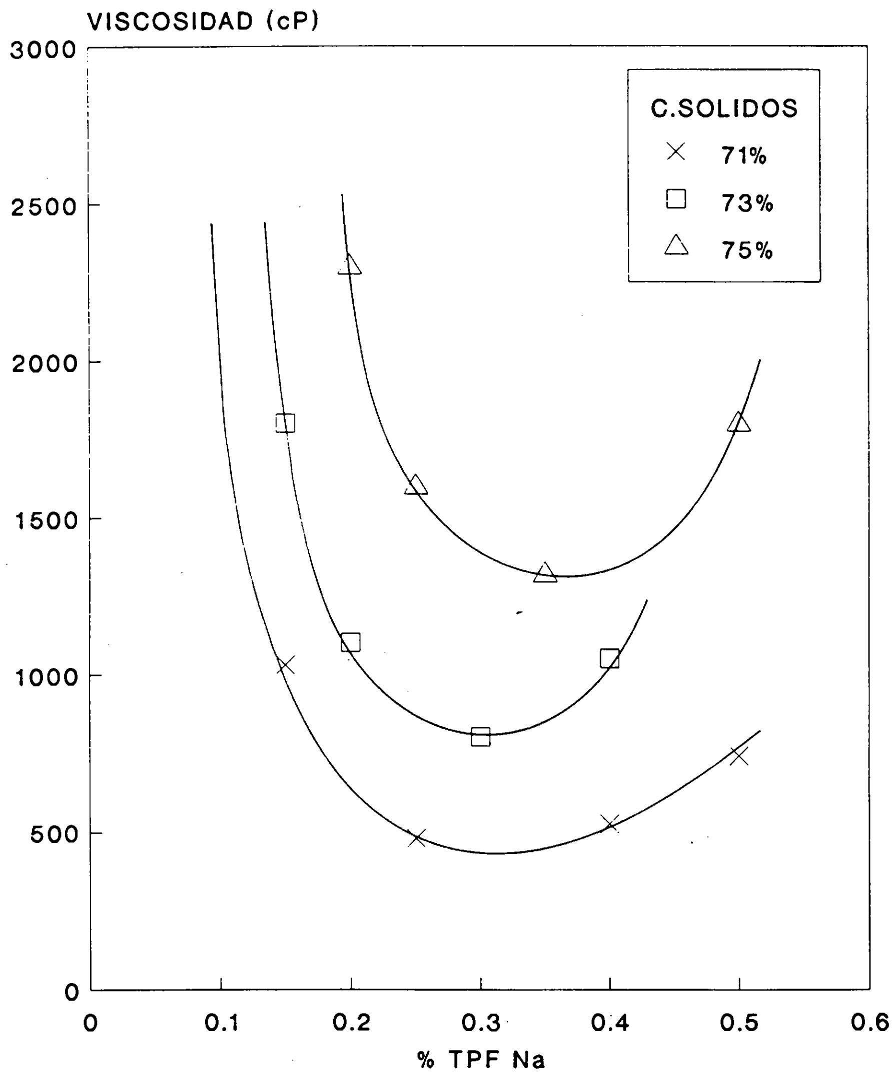

Figure 12.- Influence of the solid content of the engobe C1 suspension upon its rheological response.

Pag. 29this being essentially due to the decrease in the amount of water trying to permeate the porous layer which forms during casting. In this instance the permeability (Kp) and the porosity of the bed of particles () hardly change at all when the solid content is modified, parameter n being the factor which determines the speed at which the wall forms, and this same parameter is linked with the solid content of the suspension by means of equation [2].

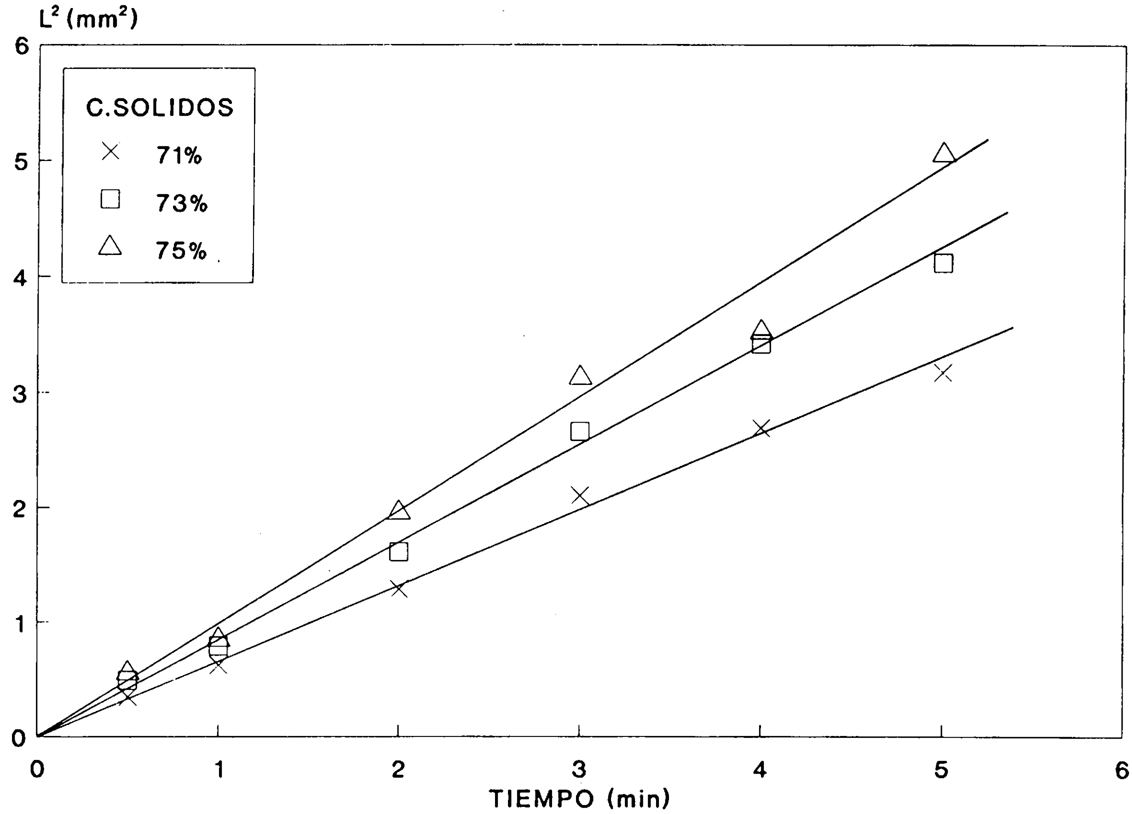

Figure 13.- Influence of the solid content of the engobe C1 suspension upon the speed which the wall forms.

5.- CONCLUSIONS

- A finely tuned experimental procedure has made it possible to determine with sufficient precision the permeability of the engobe layer and the effect of operational variables (rheological characteristics and solid content of the suspension and the extent to which the engobe components are ground) and compositional variables (content and nature of the clay) upon this permeability.

- It has been shown that the rheological characteristics of the suspension, the permeability of the layer formed and the speed at which the engobe wall forms, due to a close relationship with the percentage and size of the colloidal particles, depend considerably upon the nature and percentage of plastic materials present in the composition.

- In the case of particularly deflocculate engobe suspensions, it has been observed that the permeability of the layer formed is inversely related to the specific surface of the composition.

- The extent to which the engobe is ground, which modifies the agglomeration of the particles of the layer formed during its application on a ceramic body, affects the permeability of the layer formed and as a consequence the speed at which the wall of the engobe is formed. Nevertheless, this effect has only been noted when comparing suspensions with very different rejections.

- When the solid content of the suspension is increased, besides an increase in viscosity, the speed at which the engobe wall is formed also increases, although the porosity and permeability of the layer formed do not change.

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