THE RHEOLOGICAL PERFORMANCE OF ENAMEL SUSPENSIONS.THE INFLUENCE OF THE SUSPENSION'S PROPERTIES.

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SUMMARY

We characterized several suspensions customarily used in the ceramic subsection of floor and wall tiles. These suspensions present a wide range of viscosities which vary according to the type of application in which they are used. Generally, their performance is both thixotropic and pseudoplastic and they also have a minimum stress fluency.

We confirmed that at high velocity gradients of deformation, the viscosity is related to the volumetric fraction of suspension solids and their maximun packing according to the Krieger-Dougherty equation.

Lastly, we studied the effect of the deflocculation state, of the type of clay mineral, and of the different additives on the rheological performance of these suspensions.

1.-INTRODUCTION

The application of engobes and enamels used in the manufacture of floor and wall tiles is generally done using concentrated suspensions.

The rheological performance of this type of suspensions cannot be considered Newtonian. The suspension's viscosity is not a constant characteristic , but depends instead on the velocity gradient of the wire cutter and the rest time, or on the application of deformation to those that have been subjected to (= (,t)). On the other hand, a critical stress fluency frequently exists below which a perceptible flow is not produced. Therefore, the characterization of the rheological performance of these suspensions requires the determination of the aforementioned critical stress and the influence of the aforementioned factors on the viscosity (1,2,3,).

The rheological properties of these suspensions depends on the nature and the properties of their component elements (solid-liquid-additives), as well as on their proportions and interactions. On the other hand, these rheological properties directly influence the suspensions' performance during their application, which shows how important it is to characterize and control the suspensions correctly for the proper development of the enameling process.

2.-OBJECTIVES.

The rheological performance of concentrated suspensions has been dealt with extensively in the bibliography, both in theoretical form, as well as in applications to different industrial sectors (food technology, paints, pharmacology, etc.)Nonetheless, few specific publications (2,4,5) exist that apply experimental procedures and up-to-date information to the study of suspensions that are used in the enameling of ceramic tiles.

As a result of a great interest in the rheological characterization of enamel suspensions in a relevant format and of the lack of existing information on the subject, we planned the current study with the following objectives:

1.- The rheological characterization of industrial suspensions normally used in the enameling process and their relationship with the performance during application.

2.-The influence of the suspension properties and the different components and additives on the rheological performance.

3.-MATERIALS AND EXPERIMENTAL PROCEDURES.

3.1.- Materials.

In order to study the rheological performance of suspensions normally used in the enameling process, we selected different engobe and enamel compositions, which are used industrially in different types of application (Table I and Figure I). Accumulated Volume (%)

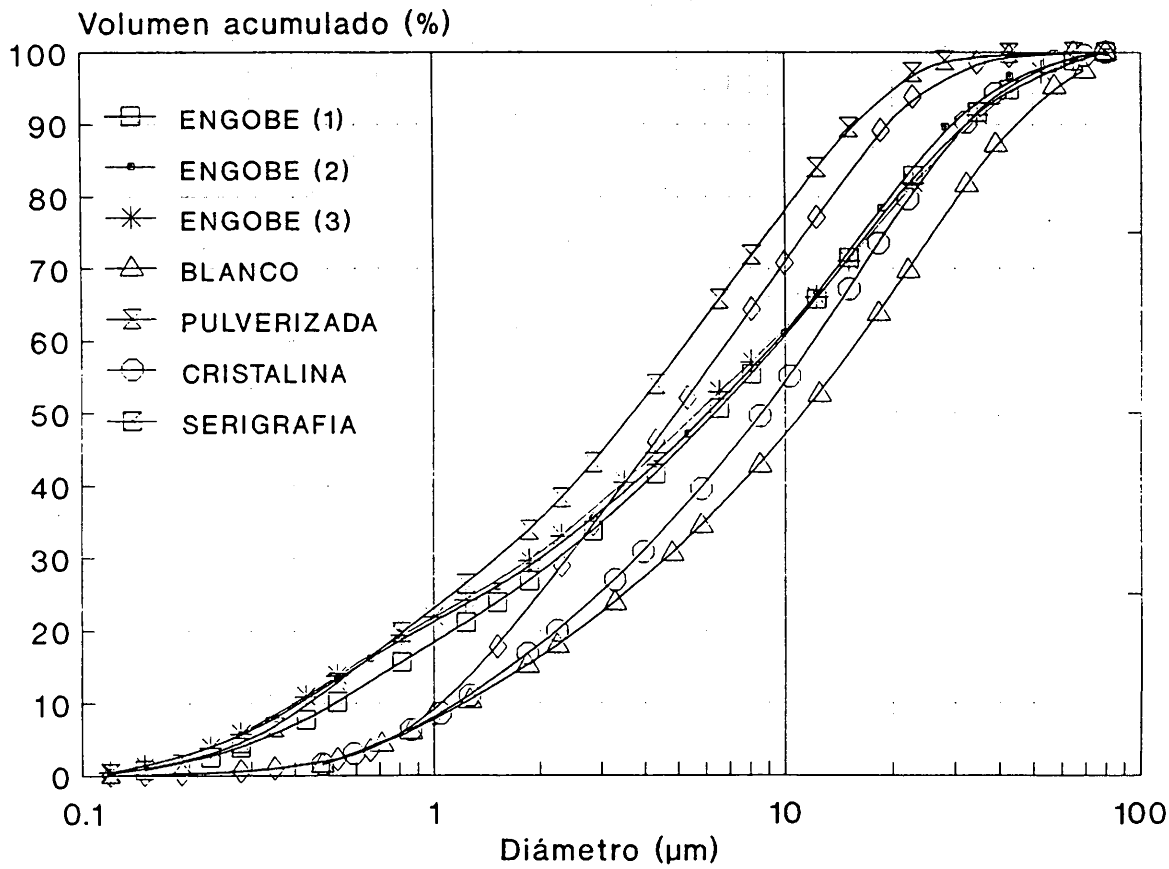

FIgure 1: The granulometric distribution of industrially used engobe and enamel compositions.

COMPOSICION	COMPONENTE PLASTICO	LIGANTE ORGANICO	TIPO DE APLICACION	C.SOLIDOS (% Peso)	DENSIDAD (g/cm^3)
ENGOBE 1	15-20% ARC.	-	DISCO	57.7	1.57
ENGOBE 2	15-20% ARC	-	CAMPANA	71.4	1.84
ENGOBE 3	15-20% ARC	-	CAMPANA	74.4	1.90
ESMALTE BLANCO	0-10% CAOL.	<0.5% CMC	CAMPANA	71.4	1.80
CRISTALINA	0-10% CAOL.	<0.5% CMC	CAMPANA	71.3	1.76
PULVERIZADA	-	-	AEROGRAFO	57.8	1.64
SERIGRAFIA	PEG	-	PANTALLA	56.1	1.66

Table,- 1. Industrially used suspensions.

On the other hand, in order to be able to study the effect of the suspension's principle properties (solids content and deflocculation state) and of the principle additives used in this type of suspensions on the rheological performance, we prepared the compositions described in Tables II and III in the laboratory.

COMPOSICION (%)	E1	E2
FRITA	25	25.5
CUARZO	25	25.5
NEFELINA	20	20.4
SIL.CIRCONIO	10	10.2
ARCILLA	18	18.4
BENTONITA	2	-

Table.- II. Engobe compositions used

COMPOSICION (%)	ES1	ES2	ES3	ES4	ES5
FRITA	100	100	100	100	100
CAOLIN	7	7	7	7	7
CMC (PM ↗)	-	0.8	-	-	-
CMC (PM ↘)	-	-	2.7	-	-
NaCl	-	-	-	0.2	-
MgCl2	-	-	-	-	0.2

Table.-III. Enamel compositions used

In order to prepare these slips, we ground the dry solid in a laboratory ball mill until a rejection of 1.5% at 40 micrometers was reached. Then we prepared the suspensions for the dilution of the solid in water or in a solution of additives.

3.2.- Experimental Procedure.

The rheological performance of the compositions we studied was determined using a rotational viscometer with concentric cylinders (3,5,6). Figure 2 shows the outlines of the experiments, or the sequence of the velocity gradients of deformation (= (t)), used in order to obtain the flow curve corresponding to each suspension. We kept the suspension at rest for six minutes in the mensuration system (=0). Next, a maximum deformation velocity (max) was reached in two minutes. Then the deformation velocity was reduced to =0 in another two minutes. An max of 800 s-1 (outline A) was used in the majority of the experiments, except for the enamel compositions containing carboximetilcellulose (CMC), in which case an max of 350 s-1 (outline B) was used.

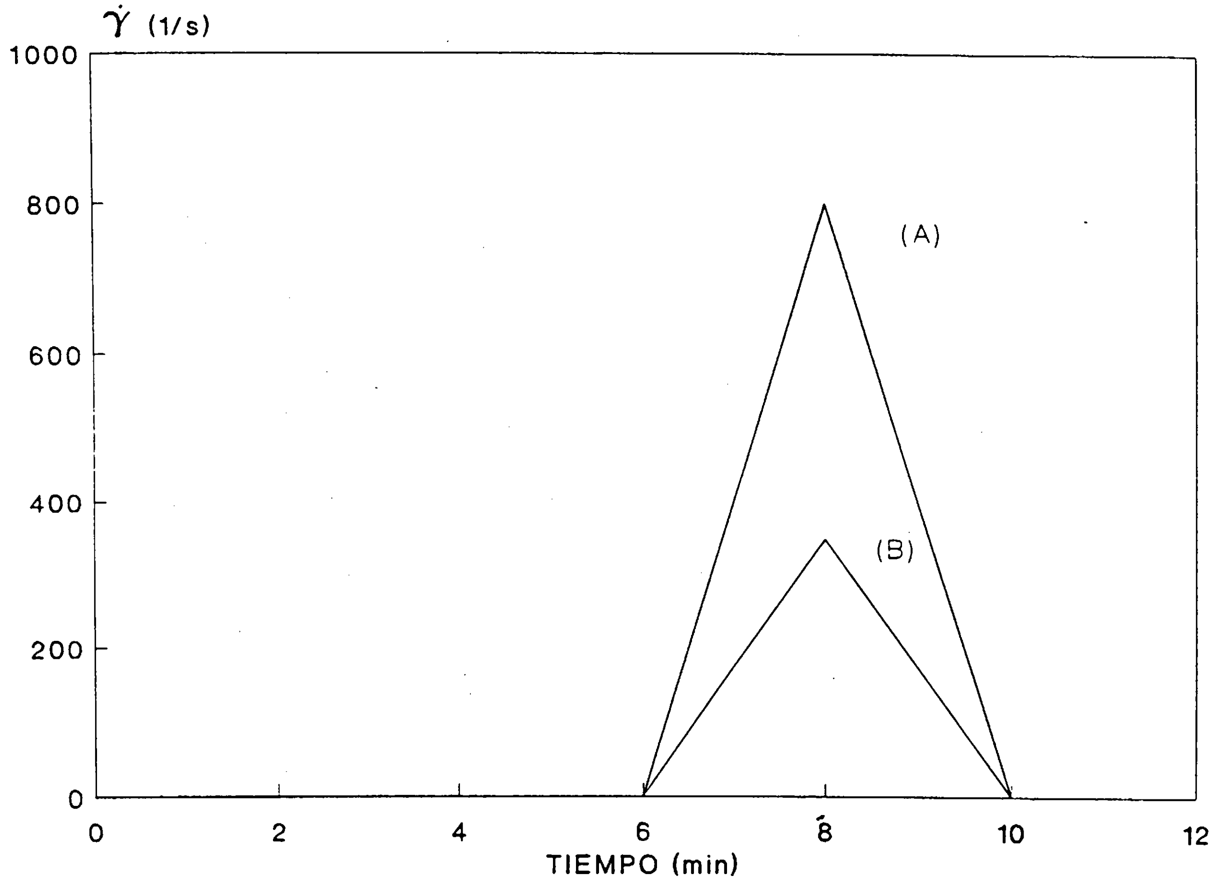

Figure 2: Outlines of the deformation velocity used to obtain the flow curves.

Figure 3 shows the calculation of different rheological parameters starting from the flow curves we obtained. The critical stress fluency, 0, is the minimum stress necessary to produce a material flow which can be detected by the mensuration system. It is easy to calculate starting from the flow curve.

The viscosity at a determined velocity gradient of deformation is the quotient between the applied stress of the wire cutter and the obtained velocity gradient of deformation. This relationship is graphically represented by the slope of the straight line that unites each point of the flow curve with zero. In Figure 3, one can observe how a material's viscosity can have different values at the same velocity gradient of deformation, depending on the prior state of agitation of the material. The thixotropy was determined as an area of hysteresis which is generated in this type of experiment (7).

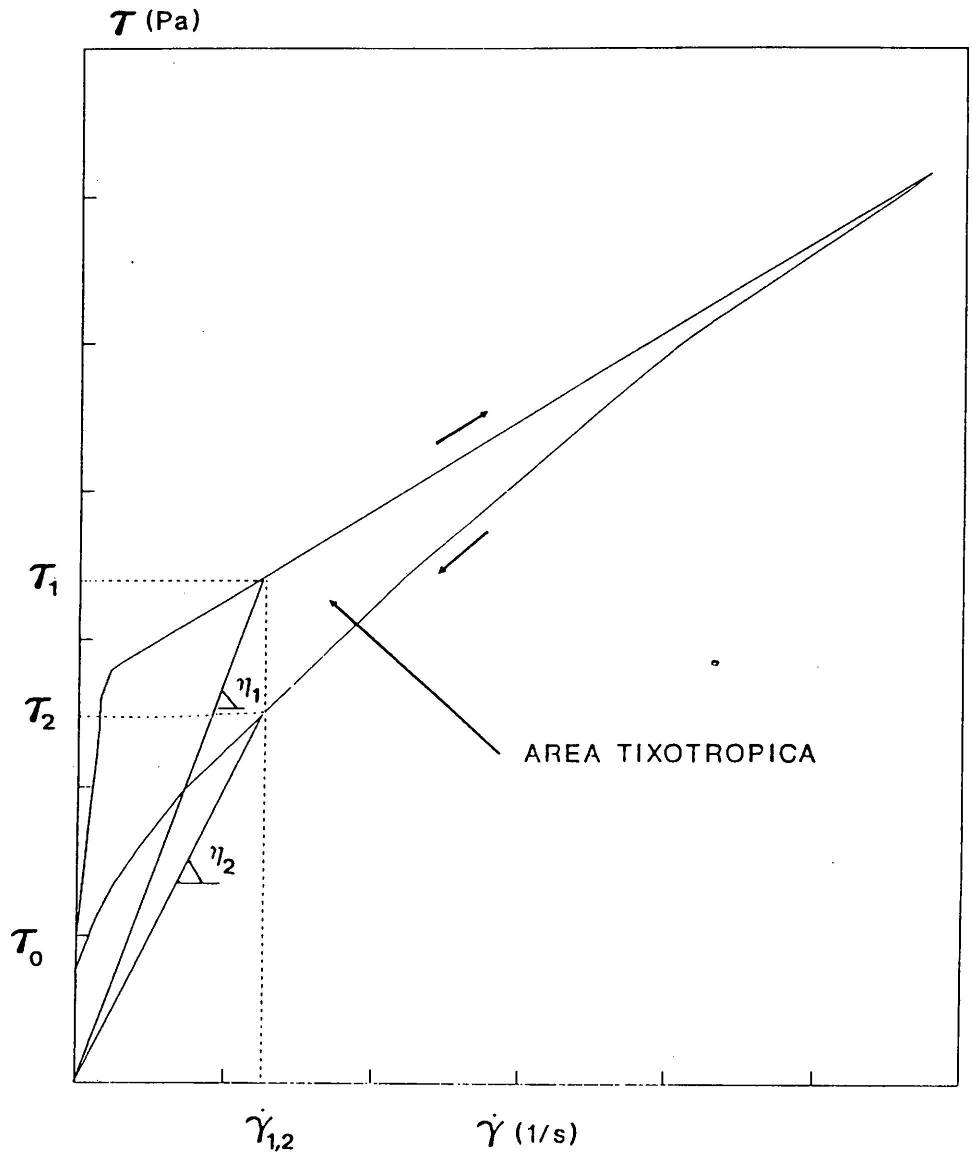

Figure 3: The calcultion of different rheological parameters starting from the flow curve.

To study the variation of viscosity with the velocity gradient of deformation in a wide range of values, a representation is normally done in logarithmic scales (Figure 4).

The volumetric fraction of suspension solids is calculated starting from the solids content (% weight) and from the actual density of the suspension's components.

Particle-size distribution is determined by laser difractometry (8). Maximum packing, m, of the solids in each suspension is theoretically determined using a modified Lee model (9).

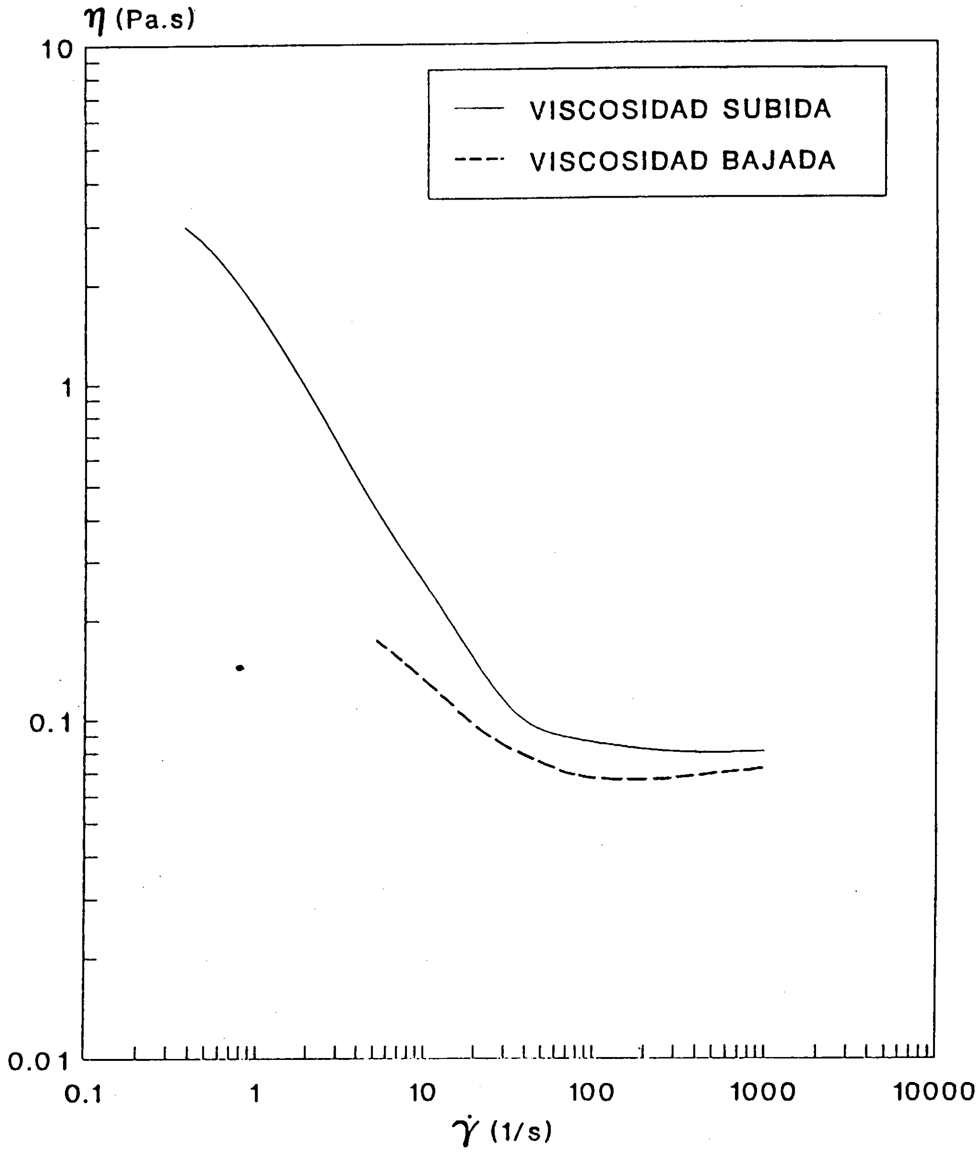

Figure 4: Graphic representation of the viscosity curve compared to the deformation gradient in logarithmic scales.

4.- RESULTS AND DISCUSSION

4.1.- The rheological performance of industrial suspensions.

The performance of enamel suspensions during their application on ceramic substrates mainly depends on their rheological properties, something which can be considered a principal factor to bear in mind in their developing and perfecting.

We have characterized the rheological behavior of different suspensions used industrially nowadays (Table IV and Figure 5), and we were able to confirm that the rheological conditions of these suspensions were determined basically by the the type of application in which they must be used, rather than by their own composition. Evidently, significant variations can exist in the performance of different suspensions intended for the same application, due to the adaptation that must be made for each individual application system.

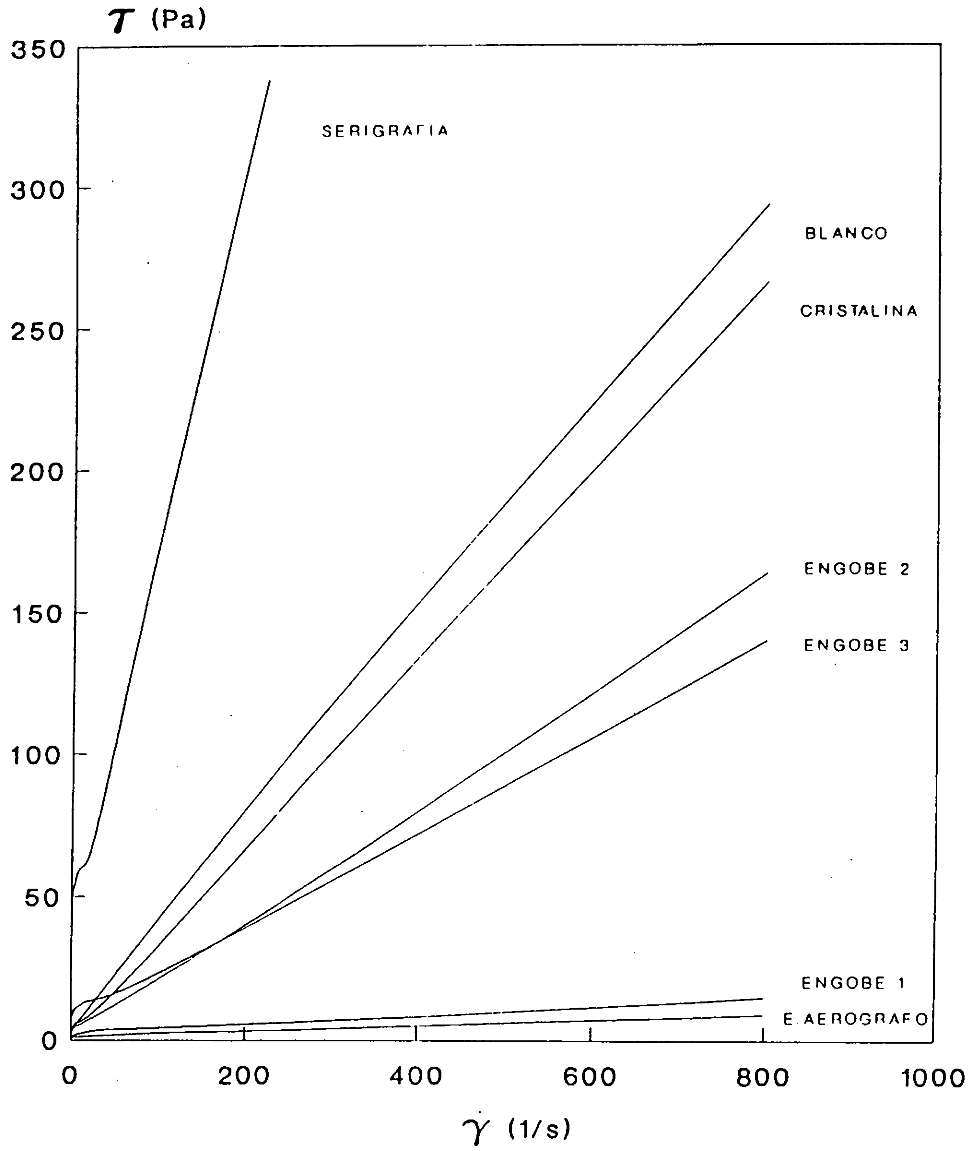

Figure 5: Flow curves obtained for different suspensions normally used in industry.

SUSPENSION	η_{∞} (mPa·s)	τ_o (Pa)	TIX (Pa/s.cm^3)	ϕ (% vol)	$\phi_{máx}$ (% vol)
ENGOBE 1	19	1.9	47.6	33.5	78.6
ENGOBE 2	198	4.5	92.3	47.4	79.2
ENGOBE 3	175	3.0	145.7	51.4	78.5
ESMALTE BLANCO	367	2.5	109.4	48.5	69.2
CRISTALINA	327	2.5	44.0	49.4	70.3
PULVERIZADA	11	1.3	7.4	30.8	76.5
SERIGRAFIA	1182	50.0	441.5	27.2	73.6

Table IV.The rheological performance of the industrial suspensions used

4.1.1- Application by curtain,

This type of application consists in dropping a "curtain" of suspension on the surface of the piece while it's in motion and it is generally created by means of a bell with an overflow level. The velocity gradients of deformation generated by this system are relatively low (50 s-1).

The viscosity of the suspensions used in this procedure has to be relatively high (( ) 300 mPa.s) in order to get a suitable hydrodynamic performance during application, a uniform distribution over the area where the bell drops, and to avoid that disturbances caused by the agitation and the falling of the suspension and/or by the line vibrations alter the evenness of the applied coat. The use of excessively thixotropic suspensions is very problematic because the variations produced over time in the suspension's properties prevent adequate application control. On the other hand, areas always exist in the bell's overflow level which are practically at rest where agglomerations of gelled material can form and then fall randomly onto the enameled pieces.

In the same manner, suspensions with a pseudoplastic performance are not recommended because of their high viscosity at low deformation gradients (difficulty in achieving a uniform surface) and because they accentuate flow differences in different areas where the bell drops.

In Figure 6, one can observe the shape of the log - log curve in the interval between 0.1 and 1000 s-1 for an engobe suspension and an enamel suspension applied using this system. In these representations, the viscosity decreases as the deformation velocity increases and an appreciable thixotropic cycle also exists. Nonetheless, the viscosity of both suspensions presents similar values for the range generated by this type of application (10-50 s-1).

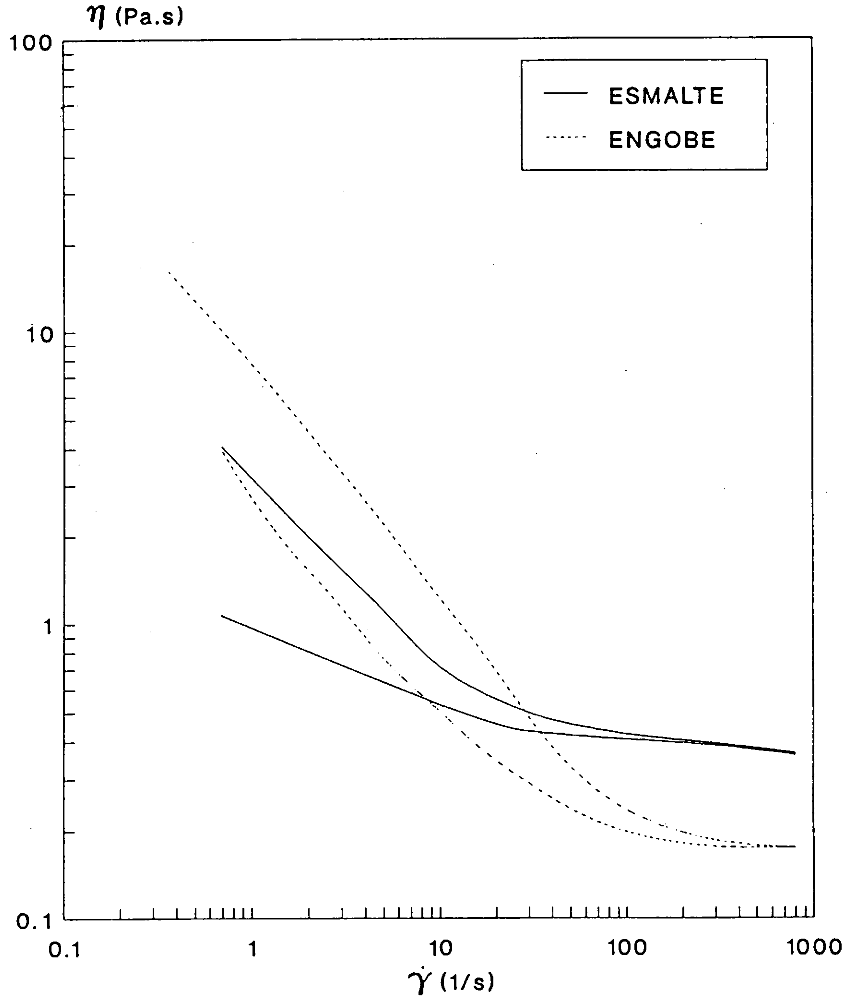

Figure 6: The viscosity curves obtained with enamel and engobe suspensions applied by curtain compared to the deformation

In the cases analized, and especially with the engobes because of their high clay content, the variation of the viscosity with the deformation velocity and with time (thixotropic area) is greater than what would be desirable for this type of application.

4.1.2.- Application by drypping.

In the case of suspensions that are applied by disk and by aerograph, it is necessary that the viscosity at high velocity gradients of deformation (10^4-10^5 s^{-1}) be low enough to allow the formation of small drops which can be extended properly on the surface of the substrate. In the cases we studied, the viscosities at high values of the velocity gradient are on the order of 10 to 20 mPa. gradient.

Figure 7 shows the variation of the viscosity compared to the velocity gradient for the "atomized" suspension and for an engobe applied by disk in the = 10 - 10 s-1 range. One can appreciate how a pronounced decrease in viscosity exists in this range as the velocity gradient increases, which corresponds to an intensely pseudoplastic performance. This type of performance allows one to obtain very low viscosities at high values, and at the same time to obtain high enough viscosities at lo values, which prevents the settling of suspension particles and therefore facilitates the suspension's stability over time.

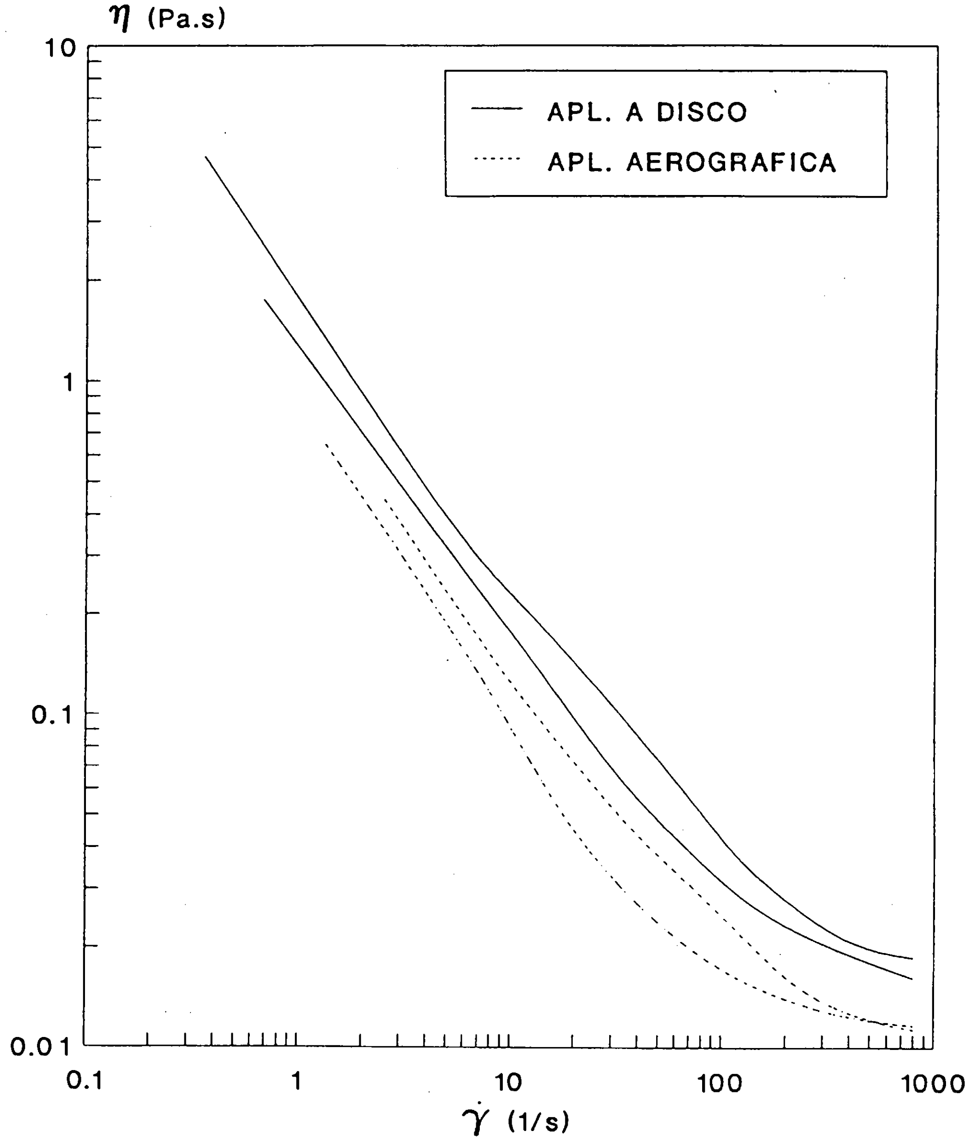

Figure 7: Viscosity curves obtained with the enamel suspensions applied by dripping compared to the deformation gradient.

4.1.3.- Serigraphics applications.

In the case of applications by slice bar, normally with serigraphic screens, suspensions with a high viscosity at rest are required to prevent liquid from dripping through the mesh before and after the passing of the slice bar, and suspensions with a low enough viscosity at high velocity gradients of deformation (10 -10 s-1) are required to permit the suspension to pass through the aforementioned mesh. On the other hand, the suspension must be stable so that the application conditions are always the same, both in time and in temperature.

In Figure 8, one can appreciate the pseudoplastic performance of this type of composition, with moderate viscosities (10^3 mPa.s) at high values and very elevated viscosities (10^5 mPa.s) for low values.

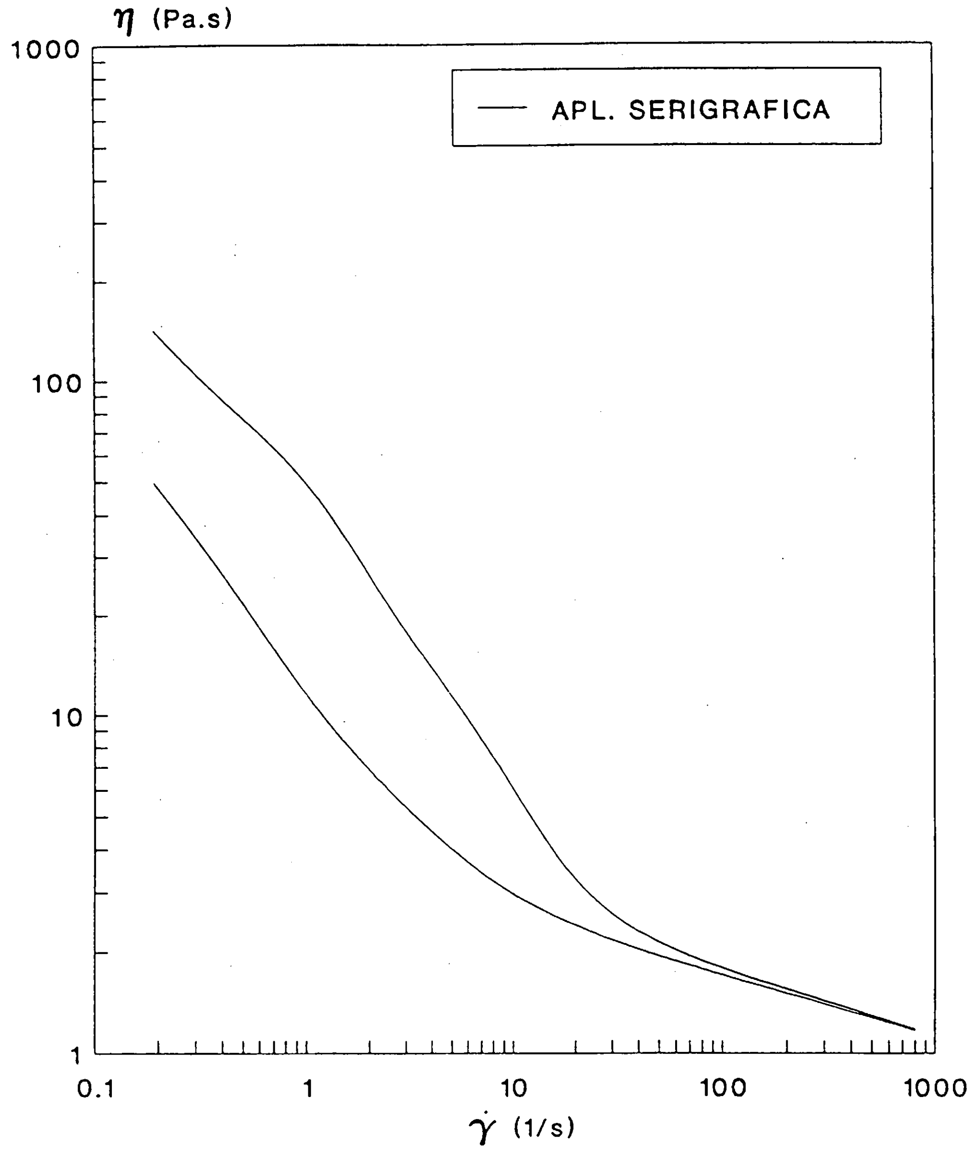

Figure 8: The viscosity curve of a serigraphic application compared to the deformation gradient.

In any case, the perfection of a suspension requires a balance of its rheological performance with the rest of the properties that affect the manufacturing process as a whole (drying time for the enamel, dry shrinkage, gas permeability, etc.).

4.2.- The influence of different suspension properties on the rheological performance.

We studied the existing relationship between the rheological performance of enamel suspensions and the suspensions' and additives' characteristics.

The study was divided into the following sections:

-Solids content.
-Deflocculation state (addition of deflocculant).
-Clay mineral.
-Organic binder.
-Flocculants.

4.2.1.-The influence of de solids content.

One of the principle determining factors of a suspension's rheological performance is the proportion of solids it contains (5). The influence of the concentration of particles on the viscosity of the concentrated suspensions must be determined in relation to their volumetric solids content, , and the maximum packing of these solids, m, (9).

The maximum solids content is defined as the volumetric fraction of solids in which all the particles are in contact and no flow is possible (infinite viscosity). The maximum solids content is determined essentially by the granulometric distribution of the material and by the shape of its particles.

There are many mathematical relations that show the variation of a suspension's viscosity compared to the suspension's solids content. One of the most widely accepted models in the Krieger-Dougherty model (6):

$$= s.(1- / max)^{-[\ ]\ max} \qquad (1)$$

: Suspension viscosity.
s: Viscosity of the suspension liquid.
: Volumetric solids content.
max: Maximum volumetric solids contents.
[ ]: Intrinsic viscosity.

In order to test the validity of this equation with the systems that interest us, we determined the rheological performance of four engobe compositions prepared with different solids contents (Table V).

C.SOLIDOS (% peso)	ϕ	τ_0 (Pa)	η_∞ (mPa.s)	TIXOTROPIA (Pa/s.cm^3)
65	0.412	<1	65	21
71	0.471	<1	220	645
72	0.483	2.5	283	840
73	0.496	4.0	381	1296

Table V. The influence of the solids content on the rheological performance.

The compositions that correspond to 71%, 72% and 73% in solids were prepared with the engobe in a maximum deflocculation state. The suspension at 65% corresponds to a partially flocculated state, with which we obtained viscosities that were apparently similar to those of the rest of the compositions. (We used a torsion thread viscometer to determine their viscosity.)

If the viscosity logarithm at elevated velocity gradients of deformation is represented as it compares to the (1- / m) relation logarithm (Figure 9), the experimental points can be adjusted into a straight line with a negative slope, just as the equation forecast, effectively proving that the said relationship complies with the systems studied.

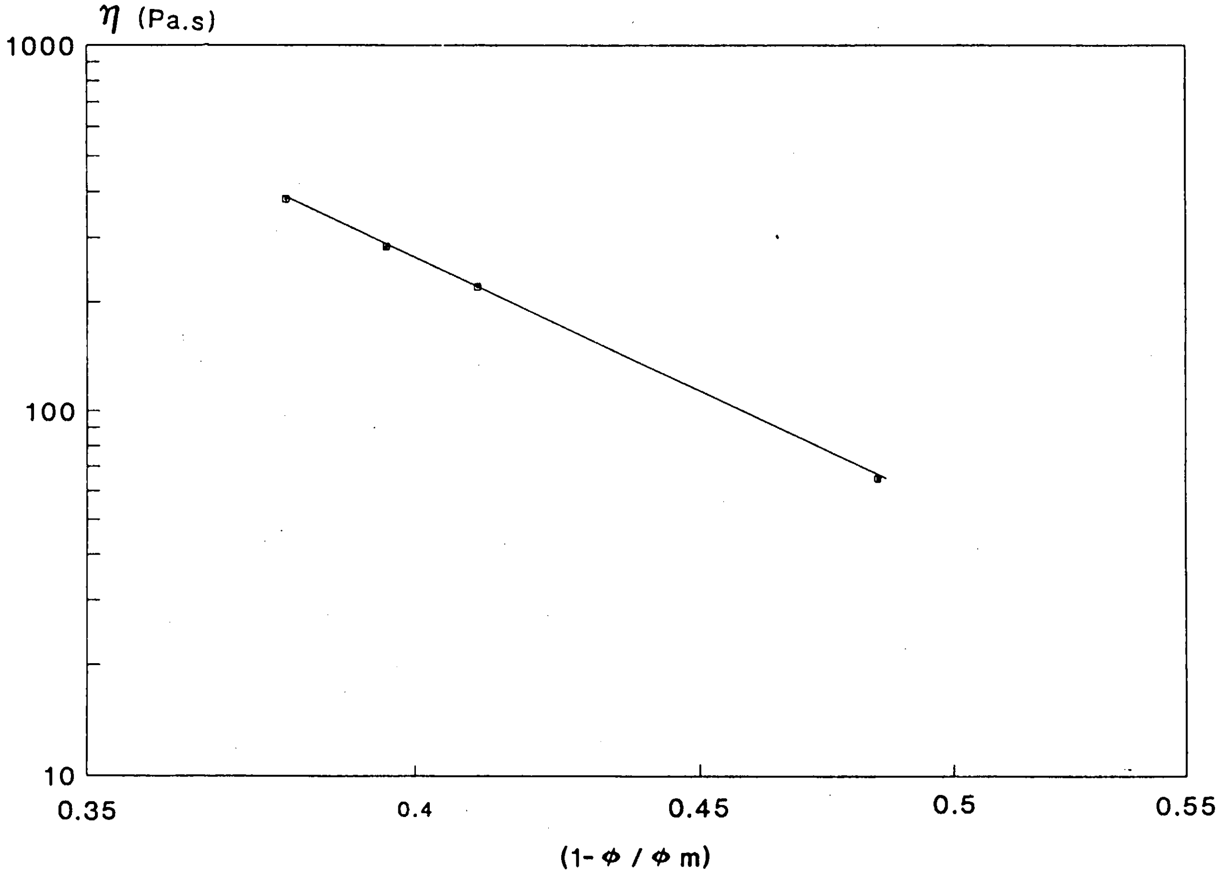

Figure 9:The variation of the suspensions' viscosity with their volumetric fraction.

In Figure 10, the variation of and the viscosity is represented for the four suspensions with different solids contents. One can appreciate that the shape of the curves at elevated velocity gradients is similar for all four, and that the viscosity in this area is directly related to their solids contents. The same does not occur for low or intermediate deformation velocities in which the agglomeration of particles has a notable influence, just as can be observed by comparing the suspension containing 65% in solids with the other far more deflocculated suspensions containing 71%, 72%, and 73% in solids. The representation of thesuspension containing 65% in solids corresponds to a more pseudoplastic performance (greater decrease in viscosity as increases) than the rest of the suspensions.

As one can appreciate in Table V, the thixotropy and the critical stress fluency were also increased slightly by the use of higher solids contents (for an identical deflocculation state) as a result of the particles' being closer together.

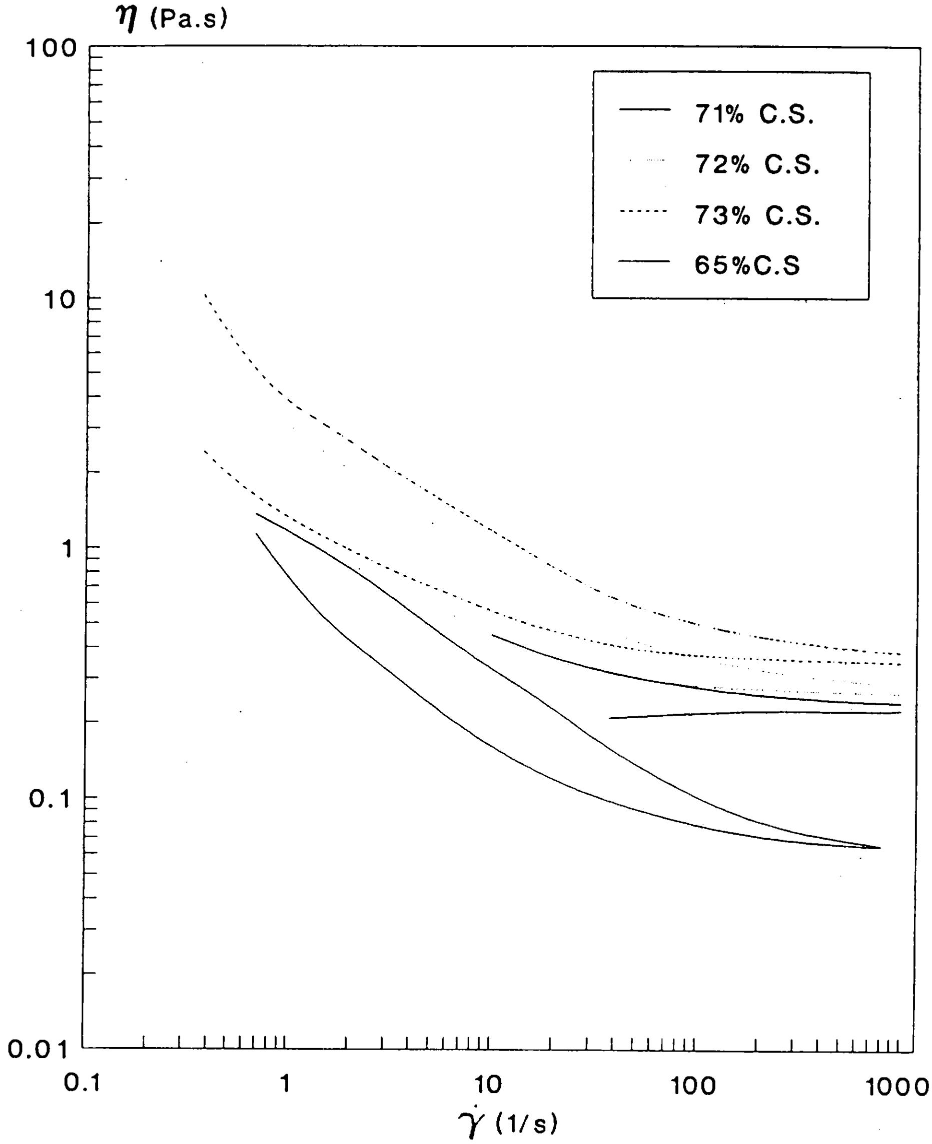

Figure 10: The viscosity curves obtained with the engobe slips with different solids contents compared to the veloci gradient.

4.2.2.- The influence of the deflocculation state..

The deflocculation state of a suspension determines the agglomeration degree of the particles it is composed of as well as the intensity of the interactions between the particles. These effects greatly influence the rheological performance of a suspension, especially for low velocity gradients of deformation.

On the other hand, the agglomerations of particles that exist in the flocculated suspensions have a poor compaction, which decreases the maximum possible volumetric solids content, m, and consequently increases the effective solids content. This increases the viscosity of the suspension. On the other hand, the interactions between the particles make the suspension properties vary over time.

In order to show these effects, we prepared the same engobe composition with different deflocculation states and we characterized its rheological performance (Table VI and Figure 11). By analyzing the results, one can gather the following conclusions:

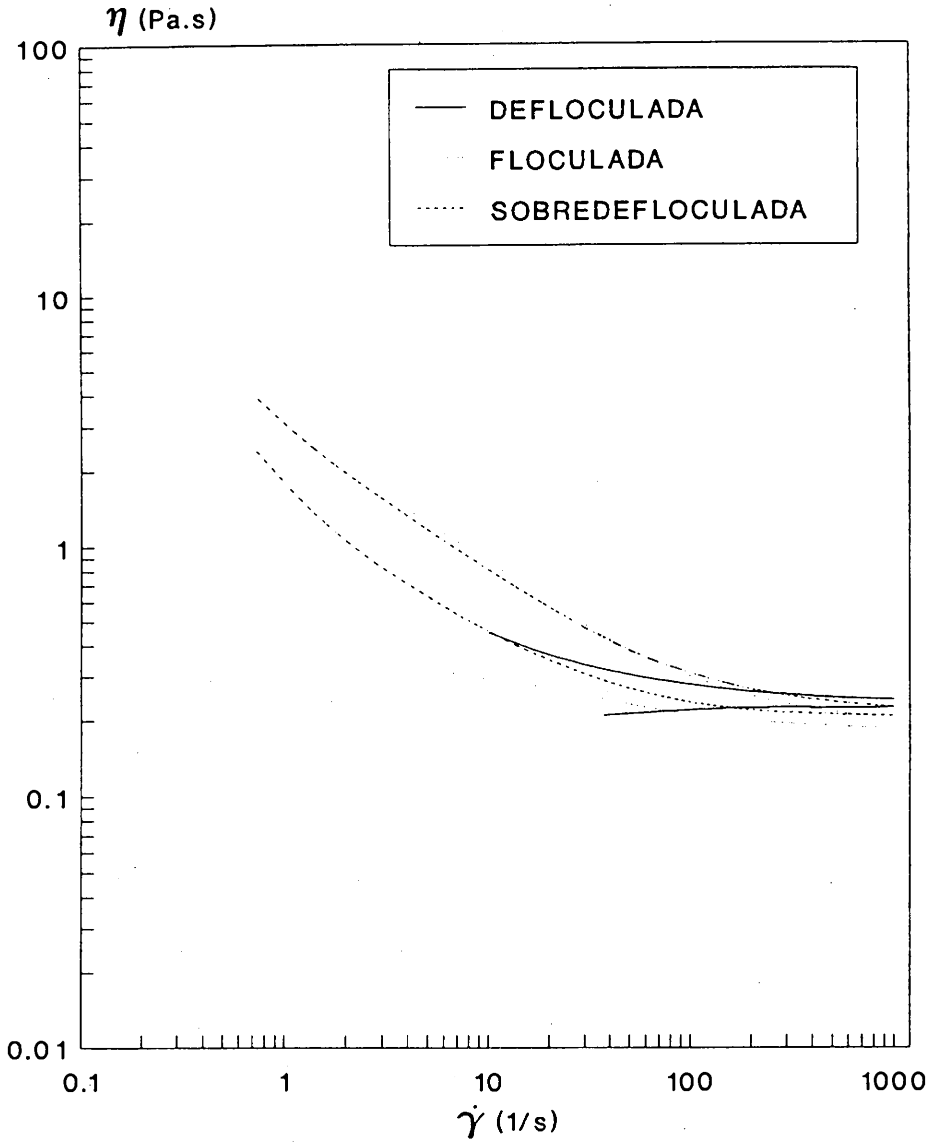

Figure 11: The influence of the deflocculation state on the rheological performance of an engobe suspension.

Defloculante (%)	η_{∞} (mPa·s)	Tixotropía (Pa/s·cm^3)	τ_0 (Pa)
0.15	220	717	3.8
0.25	199	645	<1
0.50	223	714	3.5

Table VI. The influence of the deflocculation state.

- The partially flocculated suspension presents a pronounced decrease in viscosity as the deformation velocity increases, while the viscosity remains practically constant during the descent cycle. That is to say that the suspension has a very thixotropic and moderately pseudoplastic performance.

- The deflocculated suspension presents very little variation in its viscosity in relationship to , and its performance is closer to being Newtonian than the partially deflocculated suspension, although it does have a small thixotropic cycle which is probably due to the high proportion of clay used in its composition.

- The superdeflocculated suspension presents a decrease in viscosity as the deformation velocity increases, in both the upward, as well as the downward, course. Its performance is more pseudoplastic, but less thixotropic than a partially deflocculated suspension, which is possibly due to the greater stability of the formed agglomerations.

Generally, we observed that at elevated velocity gradients of deformation (>100 S-1), the viscosity was barely modified by the deflocculation state. This is because under these circumstances the mechanical energy applied to the system is greater than the consistency of the agglomerations, since the particles are individualized. On the other hand, both the thixotropy and the minimum stress fluency decrease as the deflocculation degree increases because of the decrease in the intensity of the interactions between the particles. When the critical percentage of deflocculant is exceeded, the interactions between the particles increase again and as a reult, the critical stress fluency and the thixotropy increase.

4.2.3.-The influence of the type of clay mineral used in engobe composition.

Industrially used engobe compositions mix kaolins, clays and/or bentonites as plastic materials. In order to check the effect of the clay mineral used, we prepared the two engobe compositions specified in Table II.

We conditioned the two suspensions prepared with these compositions to their maximum deflocculation state (minimum on the deflocculation curve) by adding sodium tripolyphosphate as deflocculant. The results of their rheological characterization are shown in Figure 12 and Table VII.

Composición	η_∞ (mPa·s)	Tixotropía (Pa/s.cm^3)	τ_0 (Pa)
E1 (2% bent)	226	645	<1
E2 (sin ben)	78	295	<1

Table VII. The influence of the type of clay mineral

The use of bentonite in the engobe compositions diminishes the attainable deflocculation degree. Even though we used a greater proportion of deflocculant in order to reach the maximum possible deflocculation, both the viscosity and the thixotropy of the suspension were appreciably higher.

In order to use compositions with bentonite or with another type of clay mineral that is both very plastic and is difficult to deflocculate, one must use lower solids contents and greater additions of deflocculant than normal. Even so, one will generally get suspensions that are more thixotropic because of the lower deflocculation degree that was reached.

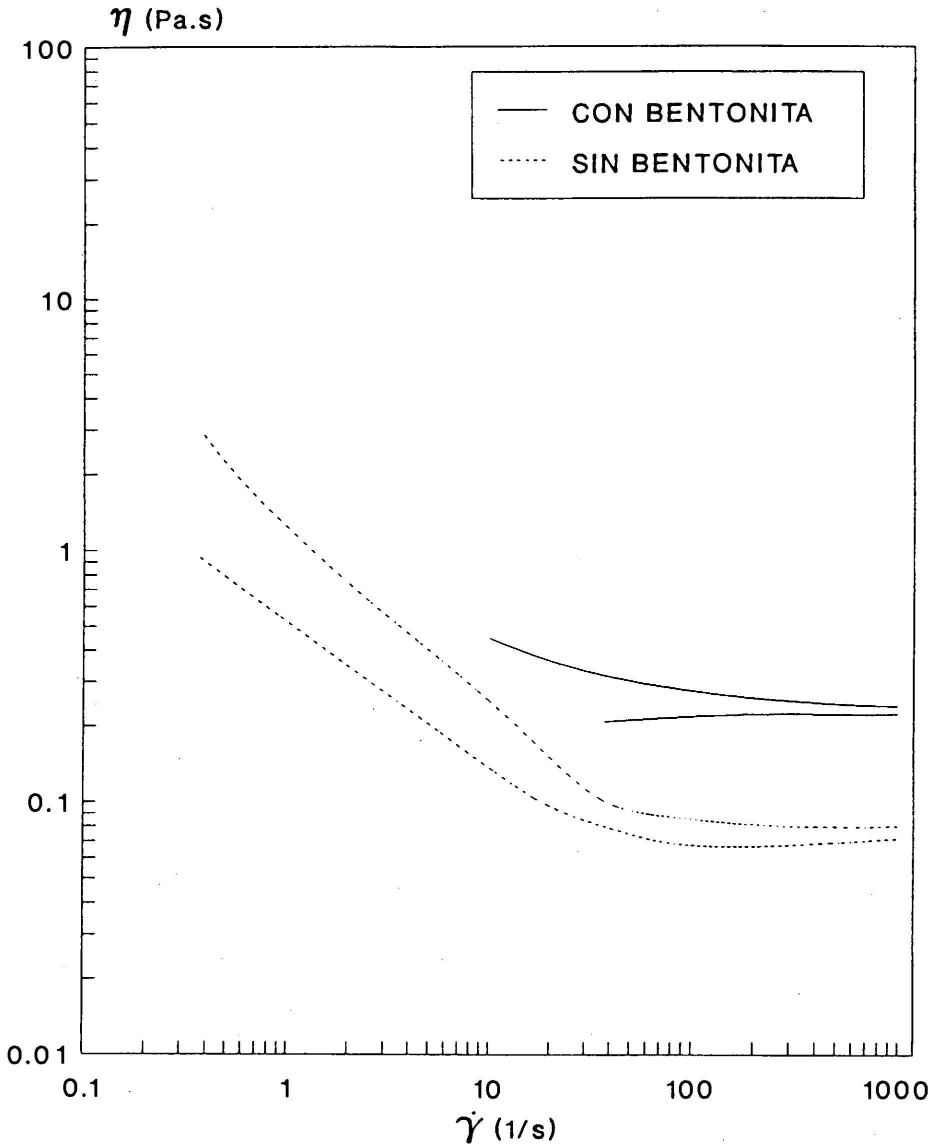

Figure 12: The influence of the type of clay mineral on the rheological performance of the two engobe suspensions.

4.2.4.- The influence of certain additives in enamel compositions.

Certain additives are normally used in enamel suspensions in order to control their rheological performance. Because of this, we prepared several compositions with some of the compounds used nowadays in the industry (Table III).

4.2.4.1.- The addition of organic binders.

In order to determine the effect of the organic binders used in industrial suspensions, we prepared two compositions with different proportions of two sodium carboximetilcelluloses (CMC) that have different molecular weights to reach an apparently similar viscosity. (We used a torsion thread viscometer to determine the viscosity.) Figure 13 shows the rheograms obtained for these two suspensions and for the reference suspension (without CMC).

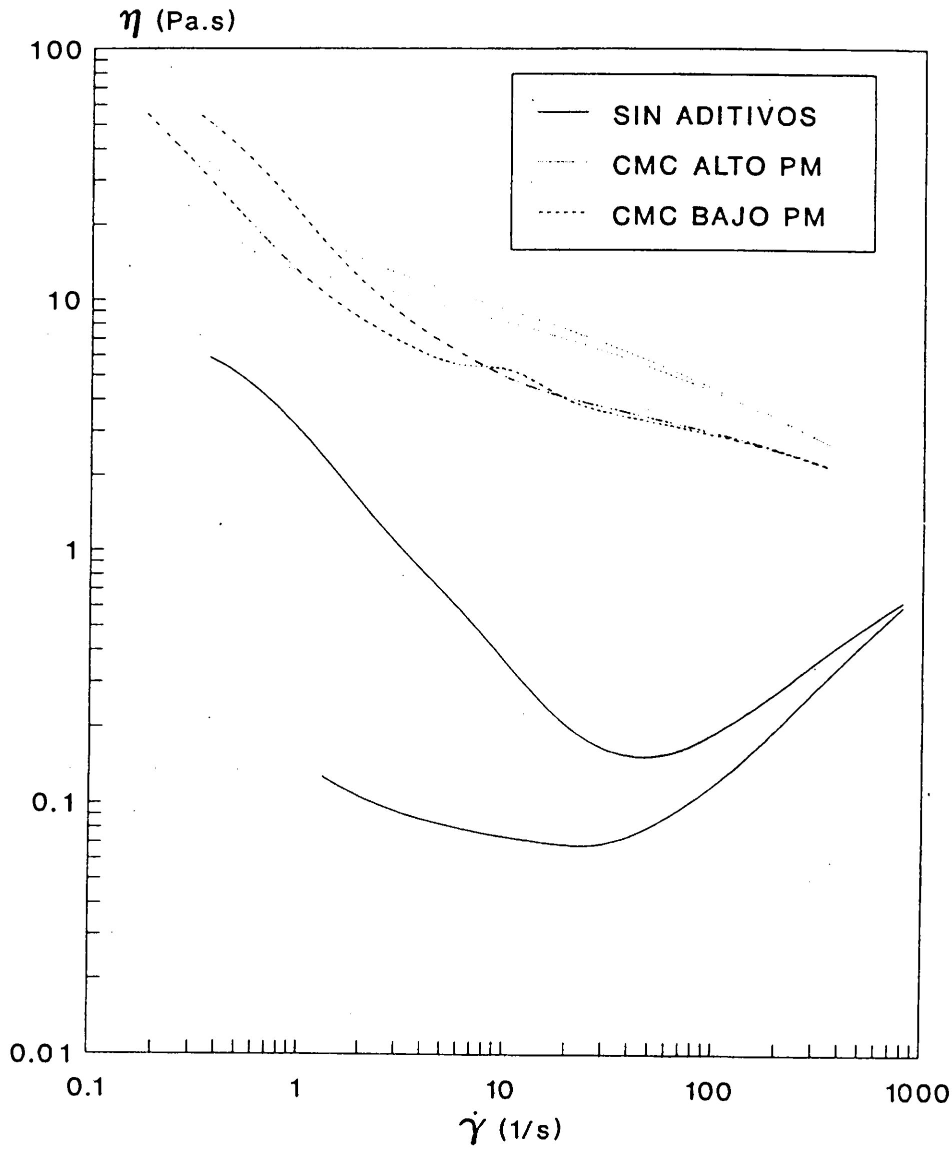

Figure 13: The influence of the organic binders' action on the rheological performance of enamel suspensions.

The reference enamel's suspension has a dilatant performance for the velocity gradient of deformation values greater than 40 s-1 because of the low proportion of plastic materials that it contains.

The addition of CMC to the suspension considerably increases its viscosity and makes its performance markedly pseudoplastic for the entire interval of deformation gradients that we tested.

Although the two suspensions with CMC were prepared with an apparently similar viscosity, the shape of the - curves varies considerably. In the case of the CMC with a low molecular weight, initially there was a sharp drop in viscosity until values between 5 Pa.s and 10 s-1 were reached and then it varied more smoothly. In the case of the CMC with a high molecular weight, the decrease in viscosity is more regular for the entire interval of values. These two suspensions perform very differently depending on the type of application they are used for, even though we measured the same apparent viscosity for several set conditions.

4.2.4.2.- Soluble inorganic additives.

We determined the effect that the soluble inorganic salts, NaCl and MgCl2, exert on the rheological performance of an enamel suspension.

In Figure 4, the variation in viscosity in relation to the velocity gradient of deformation is shown for the different suspensions studied (Table III).

The addition of NaCl to a completely deflocculated suspension barely changes the rheogram that corresponds to the ascendent, although it does change the performance of the descent.

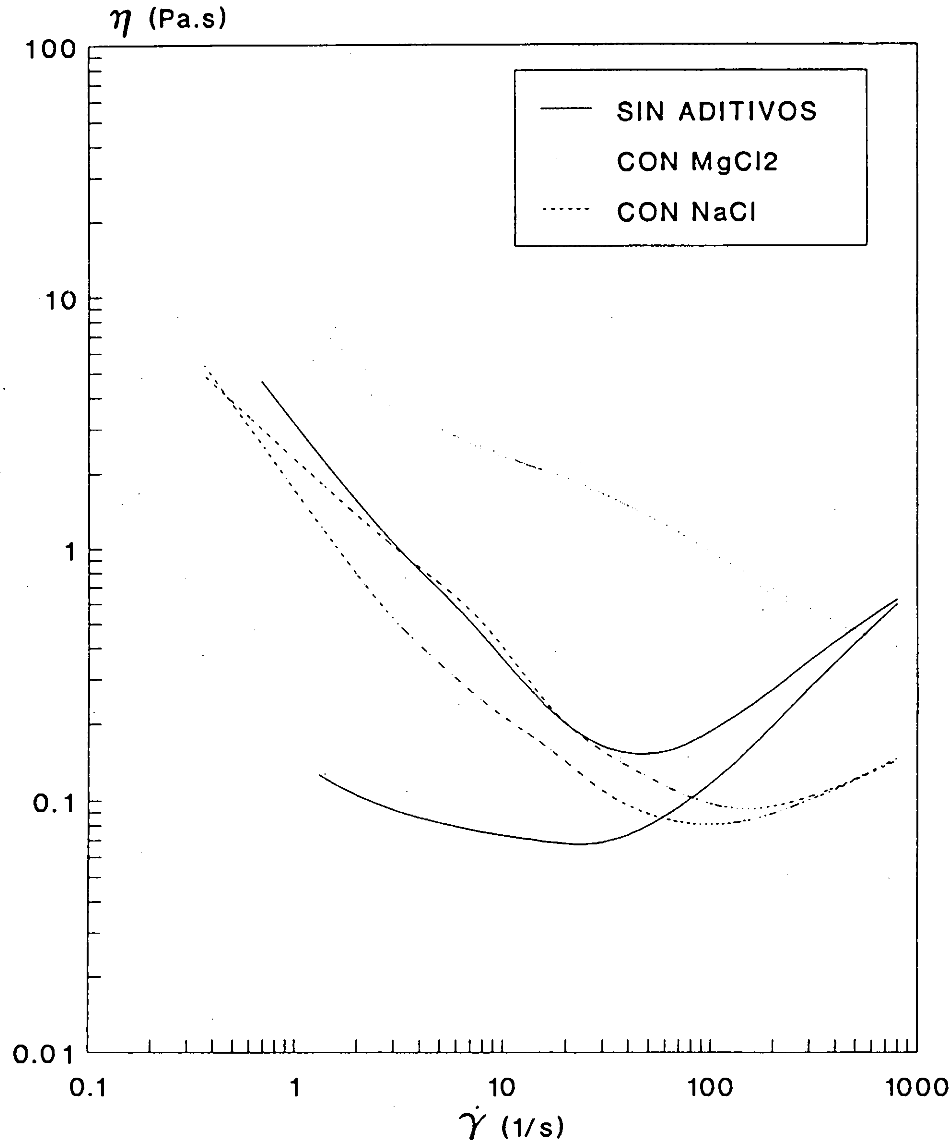

Figure 14: The influence of soluble inorganic additives on the rheological performance of enamel suspensions.

The rheogram we obtained is equivalent to a rheogram for a superdeflocculated suspension, with an acknowledged pseudoplastic, but not thixotropic, performance.

The addition of MgCl2 markedly increases the suspension's viscosity and changes its rheological performance. This suspension has a pseudoplastic performance for the entire course tested, without a single area of dilatancy. The agglomerations that formed are relatively stable, which is why no thixotropic cycle was obtained. The ascent and descent curves only separate at very low values. As was expected, the addition of a high density load anion and similar cathion exerted a strong flocculant effect.

5.- CONCLUSIONS.

We reached the following conclusions from the current study:

1.- The suspensions that are generally used to enamel ceramic floor and wall tiles present rheological performances that differ according to the type of application and the manufacturing conditions.

2.- In general, moderately high viscosities are required for application by bell and there should be a minimal variation between the viscosity over time and the velocity gradient of deformation. Pseudoplastic, and even thixotropic performances are desirable for application by dripping and by slice bar. 3.- We related the viscosity at high velocity gradients of deformation to the solids content by applying the Krieger-Dougherty equation. In this equation, the viscosity is related to the volumetric fraction of suspension solids and the fraction that corresponds to the maximum packing of particles.

4.- The suspension's deflocculation state markedly influences its rheological performance. When a state of utmost deflocculation is reached, the viscosity, the critical stress fluency and the thixotropy all decrease.

5.- The use of bentonite in engobe suspensions increases the suspension's viscosity, pseudoplasticity and thixotropy. However, if the application conditions can be fixed, these suspensions should be used with lower solids content than those that use only clay, and a greater proportion of deflocculant should be added.

6.- The use of carboximetilcellulose markedly increases the suspension's viscosity and pseudoplasticity, varying the relative magnitude of these effects with the molecular weight of the CMC.

7.- Magnesium chloride is an energetic flocculant, whereas the effect of the sodium chloride depends on the condition of the slips onto which it is applied. The addition of magnesium chloride markedly increases the suspension's viscosity and pseudoplasticity.

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