STUDY OF BUILT-UP GLAZE LAYER RHEOLOGY AND APPLICATION PROCESS BY THE ROTOGRAVURE TECHNIQUE

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ABSTRACT

In ceramic floor and wall tile manufacturing it has become increasingly commonplace to perform decorating applications by deposition of a considerable layer of glaze. This layer may be necessary for the general coating of the piece or, on other occasions, to cover very concrete, bounded regions of the product (mosaic, reliefs, etc.)

The waterfall or curtain (bell) application prevents selective coverage of regions of the tile and hence the tile decorations indicated above, thus representing a technical and aesthetic constraint in the development of new ceramic products.

The development of the rotogravure decorating technique enables performing this application, whether in terms of complete surfaces or precisely bounded regions.

For proper implementation it is necessary to know the variables that influence the process, both from the point of view of the materials (glazes and additives) and the equipment (decorating machine and related items) used.

The present paper studies the glaze variables and rheological conditions that enable effecting this type of application, as well as the variables relating to the equipment and process for correct performance by the rotogravure technique.

Glazes of different nature and several types of additives are studied with a view to defining the best working conditions for realising the desired application without any problems.

To validate the results, industrial-scale tests were conducted and the findings analysed, enabling various types of ceramic pieces with different decorations to be made.

1. INTRODUCTION

As is well known, the behaviour of a ceramic suspension is defined by multiple factors. In the case at hand, i.e., the application of a built-up layer by ROTOGRAVURE, and specifically a glaze layer, the proper performance of this type of decoration will be influenced by different variables, such as glaze rheology and the production variables that affect its application, including the machine and everything this involves, as well as the other variables proper to any production line in general.

The different variables that are considered of most influence are set out below.

1.1. SUSPENSION RHEOLOGY

Viscosity is expressed in the form of the following equation:

$$\eta = - \frac{\sigma_{yx}}{(dv_x/d_y)} \qquad (1)$$

This equation is usually written in simplified form as:

$$\eta = (\sigma_{yx} / \gamma) \qquad (2)$$

where:

$\boldsymbol{\eta} = \boldsymbol{\mu}$ = viscosity

$\boldsymbol{\sigma_{yx}}$ = shear stress $= \mathbf{F} / \mathbf{A} = \dfrac{\text{Shear force}}{\text{Area}}$

$\mathbf{- dv_x/d_y} = \boldsymbol{\gamma}$ = shear rate

Rewriting Equation (2) then gives:

$$\sigma_{yx} = \mu \cdot \gamma \qquad (3)$$

Plotting shear stress versus shear rate then yields a straight line whose slope is the viscosity, known as ABSOLUTE VISCOSITY.

Such behaviour is not general to all fluids, but solely in those termed newtonian. In other fluids, viscosity depends on stirring (shear rate).

Different types of fluids will therefore be found, according to their behaviour in relation to the parameters described.

The behaviour of the different types of fluids can be graphically illustrated as follows:

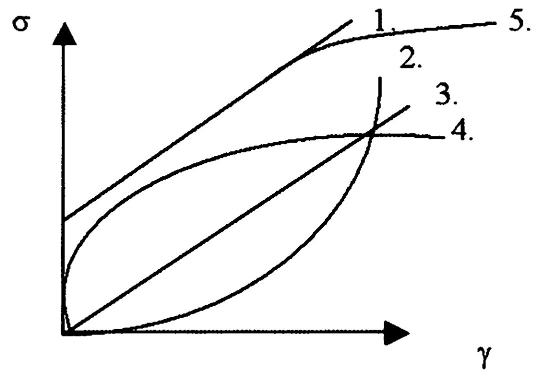


Figure 1. Types of fluids

1. BINGHAM
2. DILATANT
3. NEWTONIAN
4. SHEAR THINNING
5. GENERAL PLASTIC

Each of these behaviours leads to a different fit in the graph of the rheological analysis data.

The general equation that regulates the different rheological behaviour is:

$$\sigma = \sigma_o + K \cdot \gamma^n \qquad (4)$$

where γ is the applied "shear rate", σ_o is "threshold yield stress", **K** is the so-called "consistency index" and **n** is the "flow index".

On the other hand, there is a further type in addition to the above, termed THIXOTROPY, in which viscosity depends on time as well as on shear rate. From a theoretical point of view, this can be defined as the area enclosed by the curve plotted between the shear stress and the shear rate applied in a test in which the shear rate increases progressively, and then proceeds in reverse form:

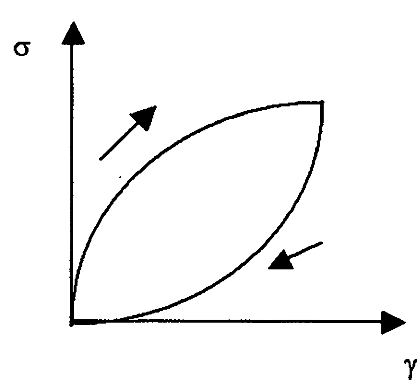


Figure 2. Thixotropy

1.2. PRODUCTION VARIABLES

a) Roll

The type of silicone used will be type T1 or INTERMEDIATE, the type being the different "graphic mask" depending on the grammage to be applied.

Obviously, the intaglio "track" on the roll (mask) will also produce a deposition of the suspension in the form of "ridges" or "waves", which will need to be eliminated in order to obtain a perfectly smooth (stretched) layer:

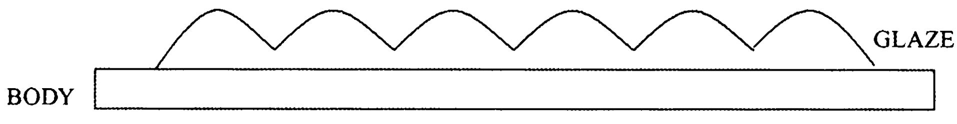


Figure 3. Application

b) Machine

- Pressure of the roll on the piece.
- Blade angle of attack.
- Deck travelling rate (tile speed).

c) Suspension:

- Drying time of the applied glaze layer: time in which the applied layer can regulate final glaze stretching, before becoming a static solid layer. This will depend on:

  - Application temperature (body-engobe system).
  - Blade angle of attack.
  - Deck travelling rate (tile speed).

- Glaze rheology: Viscosity and Thixotropy especially at low shear rates (practically at rest) owing to their effect on the elimination of the "waves" produced by the application.

- Glaze melt viscosity during firing of the applied layer.

In particular, the key variables studied have been the application **temperature** (tile), **solids content, type of vehicle, and rheology** of the suspension, in this case involving a glaze.

These data are obviously references in the unfired state, but as an optimum application of the layer is to be obtained by firing, the firing process will also have its effect (viscosity melt); however previous experiments have shown that the variables relating to the unfired state have a greater impact.

1.3. OBJECTIVES

- Studying the process variables that influence the application of built-up layers by the rotogravure system.

- On the base of the optimization of the studied variables, performance of glaze applications by rotogravure on different types of products: mosaics, geometric borders, smooth pieces, smooth body with bas-reliefs (holes), etc.

2. EXPERIMENTAL

2.1. MATERIALS

First, the work focused on both red and white-firing ceramic bodies in a standard tile firing cycle. The pieces were fired in a "KEMAC" single-deck roller kiln.

Conventional electric laboratory ovens were used to heat the pieces.

The rheological measurements were performed with a HAAKE rheometer with Z34 DIN Ti sensor.

Different ROTOCOLOR rotogravure machines were used to perform the applications.

The roll used was of the INTERMEDIATE type with ERG26 mask.

The tests were conducted using conventional ceramic glazes and additives.

2.2. METHOD

As the rotogravure decorating inks already have quite well-established physico-chemical and rheological characteristics, it has been attempted to parameterize the work based on these characteristics applied to a given glaze, to enable easy glaze preparation and rheological conditioning for correct application by the rotogravure system.

For this, a normal bell glaze was used to study the different process variables that influence this type of application, then rheologically conditioning the glaze by adding vehicles with characteristics resembling those generally employed in standard rotogravure decorating inks.

Using a conventional vehicle for this type of application with a bell glaze suspension, a suitable glaze has been prepared to study the influence of drying time on the glaze layer.

Subsequently, selecting different types of frits a series of glazes has been prepared and characterized rheologically (viscosity and thixotropy) with a view to establishing a relation between these parameters and the quality of the application.

Finally, after determining the influence of the studied variables, a suitable vehicle has been developed for this type of built-up applications.

The work method followed has been relatively simple:

- determination of the rheological data of a conventional glaze for a bell application ("CONVENTIONAL GLAZE").

- rheological conditioning by introducing additives into the glaze composition ("CONDITIONED GLAZE").

- determination of the rheological data of the conditioned glaze.

- application of the glazes by the rotogravure machine on the body engobed by gunning, with a tile temperature of 60ºC.

The laboratory-scale studies were completed by pilot plant and industrial-scale trials.

3. RESULTS AND DISCUSSION

The present study has focused particularly on the application in the unfired state, since it is obvious that the final aesthetic effect will largely depend on this application.

In the study a series of variables has been kept constant, such as machine adjustment, type of roll, type of deflocculant, type of kaolin and suspension particle size.

3.1. INFLUENCE OF **DRYING TIME** OF THE APPLIED GLAZE LAYER

This variable is influenced by the following parameters: application temperature, layer or weight of the applied glaze and glaze solids content.

For this study, a conventional bell glaze was used to which a conventional vehicle was added for rotogravure application, in order to achieve a typical viscosity in this type of application of 25 seconds in a **4 mm** Ford cup.

a) Temperature and glaze layer or deposited weight

One of the factors that affects glaze layer drying time is the moisture content of the body-engobe system.

In principle, the moisture of the body-engobe system at the moment of the application depends on the types of materials in the composition making up the body and the engobe.

In addition, body temperature at the moment of the application will make the moisture content of this system larger or smaller; the higher the temperature of the body, the lower is the moisture in the body-engobe system and therefore the faster will the glaze layer dry.

In view of these results, an excessively high body temperature at the moment of application will be unsuitable, as it will impair the desired aesthetic result.

WEIGHT (P_A>> P_B)	TEMPERATURE (ºC)	DRYING TIME (sec)	APPLICATION(1)
P_A	90	8	6
	60	20	10
	30	40	10
P_B	90	3	4
	60	11	8
	30	30	10

Table 1. Influence of temperature and applied weight.

(1) "Stretched" glaze layer application by rotogravure: Incorrect<5; Correct=10, in the unfired state.

b) Influence of solids content: Water/vehicle addition ratio.

The objective in glaze preparation for application by the rotogravure system is to obtain the highest possible density and solids content at a given viscosity, which must be between 20 and 30 seconds measured in **4 mm** Ford cup.

This requires appropriate preparation of the glaze before conditioning it rheologically for application.

In principle, as layer drying time is an important variable, it is necessary to consider that the water content in the glaze composition in milling will not only determine final glaze rheology but also drying time of the applied layer.

In addition, it is of interest to add the minimum amount of vehicle required to reach the optimum rheological state for application, and to have the fewest possible problems of glaze stability in production: rheological changes caused by water evaporation, excessive "dry-up" on the roll, pumping problems, etc.

Table 2 sets out the results obtained in this part of the study.

NORMAL GLAZE				CONDITIONED GLAZE			
WATER (%)	HEXA (%)(2)	CS (%)	DENSITY / VISCOSITY	VEHICLE ADDITION (3)	DENSITY / VISCOSITY	DRYING TIME	APLICATION(3)
25	0,15	75	1,90 / 140"	17%	1,70 / 25"	1 min 10 seg	10
30	0,15	70	1,85 / 90"	11%	1,72 / 25"	40 seg	10
35	0,15	65	1,75 / 60"	6%	1,68 / 25"	25 seg	< 5
40	0,15	60	1,65 / 35"	3,5%	1,65 / 25"	10 seg	< 5

Table 2. Influence of solids content on the water/vehicle ratio.

The results show that the required quantity of vehicle will depend on the degree of glaze deflocculation in relation to the amount of milling water. If there is too much water, this will require a smaller amount of vehicle, so that the layer will dry too fast and the application will be inappropriate, in addition to density being too low. If there is too much vehicle, drying will take too long, in addition to having a higher vehicle cost.

Therefore, there should be an optimum quantity of vehicle around 10-15% by weight in respect of the prepared liquid glaze.

3.2. INFLUENCE OF THE **RHEOLOGICAL CHARACTERISTICS** OF THE APPLIED GLAZE LAYER

a) Influence of THIXOTROPY and VISCOSITY at low shear rates

It can logically be intuited that the two rheological variables to be evaluated in this type of applications are THIXOTROPY and VISCOSITY. In fact, it has been

(2) Sodium hexametaphosphate (deflocculant).

(3) These are % with respect to the weight of the liquid glaze of solids and water.

determined that the important viscosity values for explaining the behaviour of the glaze subsequent to application lie between 0 and 1 s^{-1}.

Observing the physical deposition of the glaze by the roll on the tile, it can be intuited that at the moment of application, the value of viscosity at low shear rates will be the influencing factor, whereas after that precise moment, the value of thixotropy will determine the degree of "stretching" of the surface.

Table 3 and the Figures 4 and 5 set out the different rheological behaviours of different types of glaze compositions and preparations.

MATERIAL	P18	P19	P20	P21
FRIT 1	93	-	93	-
FRIT 2	-	93	-	93
VEHICLE (4)	-	-	28	28
VEHICLE (5)	28	28	-	-
ANTIFOAMER	5	5	5	5
WATER	30	30	30	30
VISCOSITY (sec)	28	28	28	28

Table 3. Preparation of different glazes

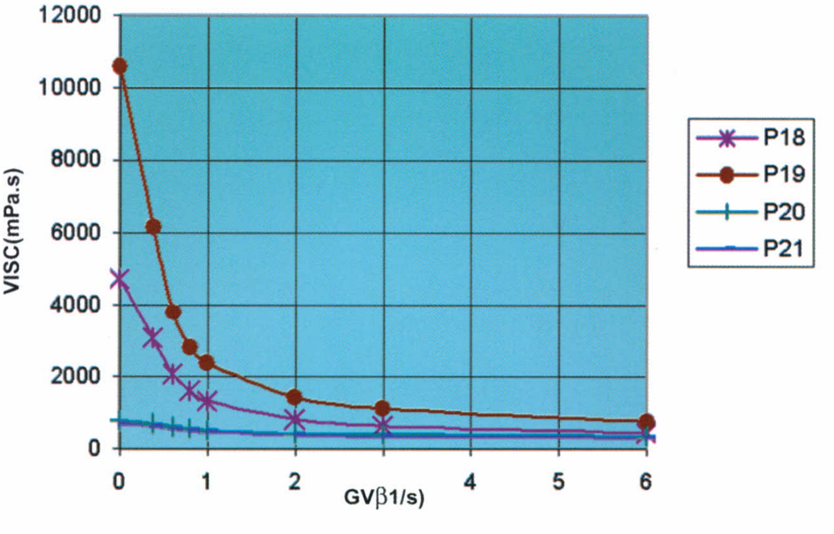


Figure 4. Rheological curves at low shear rates.

(4) Addition of the vehicle with vigorous stirring for 4-5 minutes.

(5) Addition of the vehicle with gentle stirring.

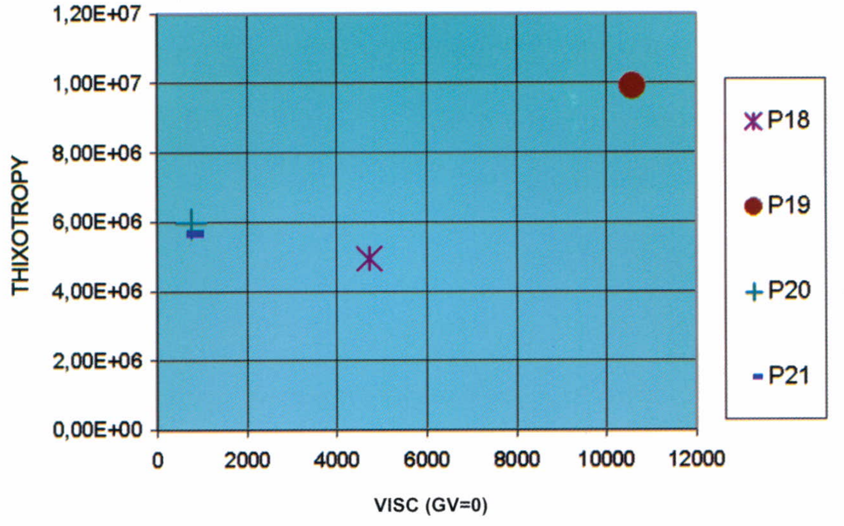
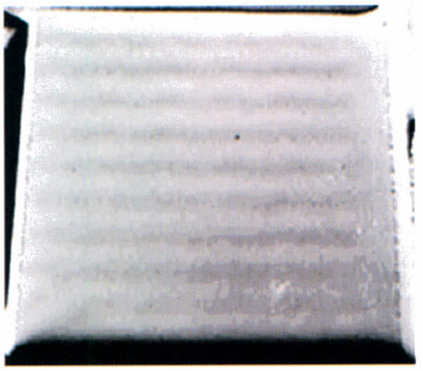
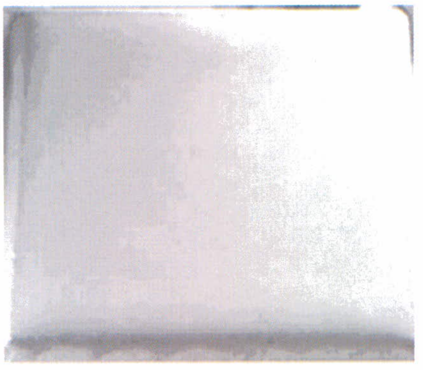


Figure 5. Thixotropy versus maximum viscosity at low shear rates.

As an example, Figures 6 and 7 show application effects that occur depending on the type of rheology.



P19 (Improper application)



P21 (Proper application)

Figure 6 and 7. Relation between the type of rheology and the appearance of the glaze application.

As may be observed, the glazes that exhibit lower viscosity and thixotropy values at low shear rates yield better results on application (better "stretching").

b) Influence of milling

The rheological behaviour was compared of a conditioned glaze, simply mixing by gentle stirring, and the same conditioned glaze with mixing by vigorous stirring or milling for about 4 or 5 minutes.

For this, THIXOTROPY has been plotted versus the maximum VISCOSITY values at low shear rates.

The influence of milling on rheology can be observed in Figs. 4 and 5 in the pairs of points P19-P21 and P18-P20. These show that when gentle stirring is applied (P19 and P18), the glaze displays higher rheological values (viscosity and thixotropy) than when the glaze is vigorously stirred or milled (P21 and P20).

In addition, it can be appreciated that the rheological differences between this type of glaze (in this case crystalline glazes) decrease in the case of vigorous milling (P20 and P21).

c) Influence of the type of frit/glaze.

At this point, a comparative rheological study is set out between different glaze suspensions before adding the vehicle for the rotogravure application. The tested glazes were a transparent glaze, a zirconium white and a matt glaze.

The data obtained are presented below.

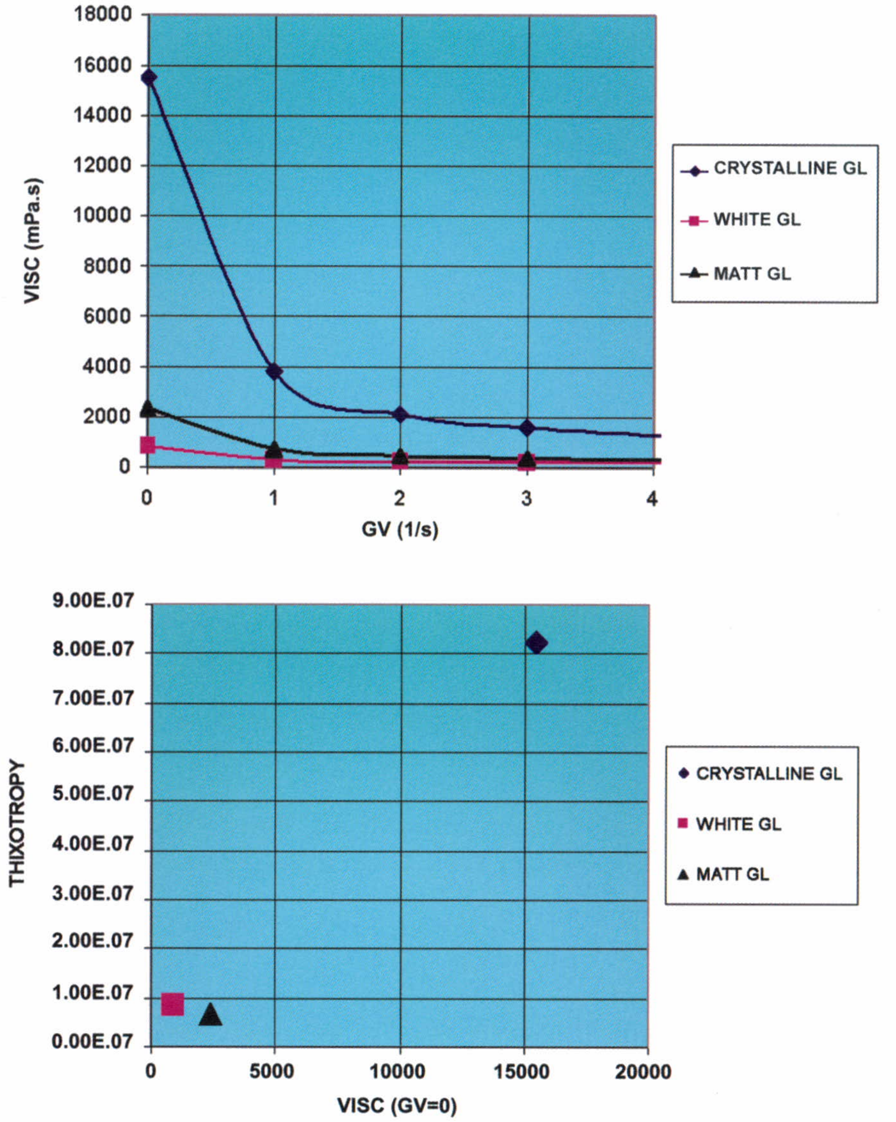


Figure 8 and 9. Comparative curves of rheological behaviour between different glazes.

Observing the results it can be stated that the crystalline-type glazes will be more complicated to apply by rotogravure, and that the matt and white glazes will be easier to condition rheologically with additives.

d) Vehicles for rheological conditioning

On the other hand, it is obvious that the influence on drying time of the applied glaze layer and the rheology of the glaze will also depend on the additives used in rheologically conditioning the glaze for rotogravure application.

The objective of the preparation is to obtain a viscosity between 20 and 30 seconds in a 4 mm Ford cup, with maximum density and solids content, and appropriate rheological values in the glaze. This will therefore depend on the composition of the additives used.

In principle, the premises were to develop a vehicle with low thixotropy and viscosity values at low shear rates, in addition to a long drying time, to enable regulating final glaze drying time.

On the other hand, it is necessary to eliminate the bubbles generated by the addition of the vehicle and subsequent milling, for which an antifoamer is introduced.

Table 4 details the conducted tests. The rheological results obtained are plotted in Figure 10:

ADDITIVE / VEHICLE TYPE	STANDARD GLAZE (P0)	P 6.1	P 7.1	P 8.1	P 8.3
VEHICLE 2	-	10	-	-	-
VEHICLE 3	-	-	10	-	-
VEHICLE 4	-	-	-	10	10
SURFACTANT A	-	5	5	5	-
SURFACTANT B	-	-	-	-	1
FORD CUP 4 mm (sec)	191	21	30	26	24
DENSITY (gr/cm^3)	1,84	1,68	1,68	1,69	1,69
DRYING TIME	5 SEC	20 SEC	30 SEC	27 SEC	25 SEC

Table 4. Test with vehicles

The results show that from a rheological point of view, tests P8.1 and P8.3 should yield the best application, which correspond to test vehicle 4, the difference between the two tests only being the type and amount of surfactant.

As far as drying time of the applied layer is concerned, compositions have been sought that all provided a drying time of around 25-30 seconds in a 4 mm Ford cup, always effecting the applications at 55-60°C, on pieces engobed by gunning.

Logically, introducing a smaller amount of additive is more cost-effective, which is why test P8.3 was finally selected (**VEHICLE** 4 and **SURFACTANT B**), without of course discarding P8.1.

In principle the quantities of each will depend on the initial conditions of the glaze but, in principle, the amount of antifoamer is preset between 0.5 and 1% by weight of standard liquid glaze, whereas the amount of vehicle will lie between 10 and 15% by weight.

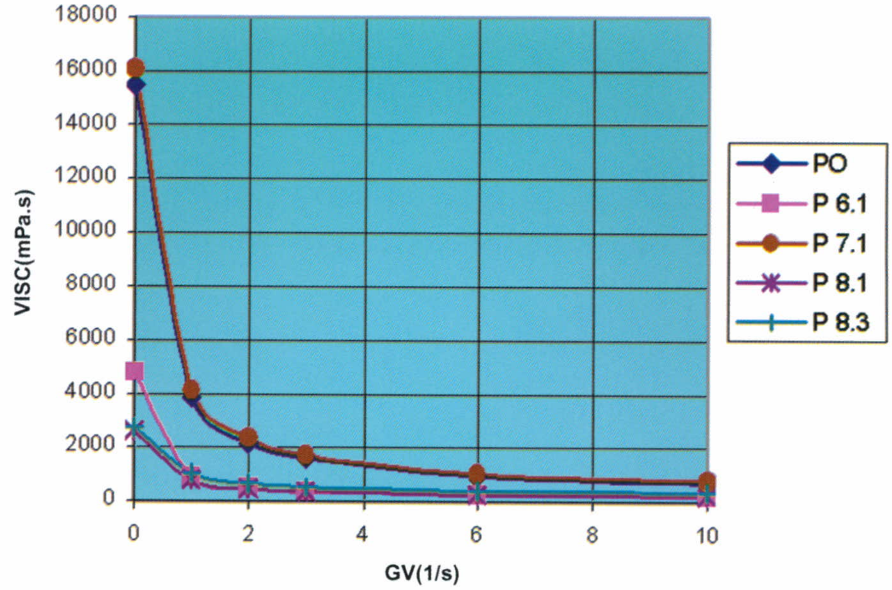


Figure 10. Rheological curves at low shear rates

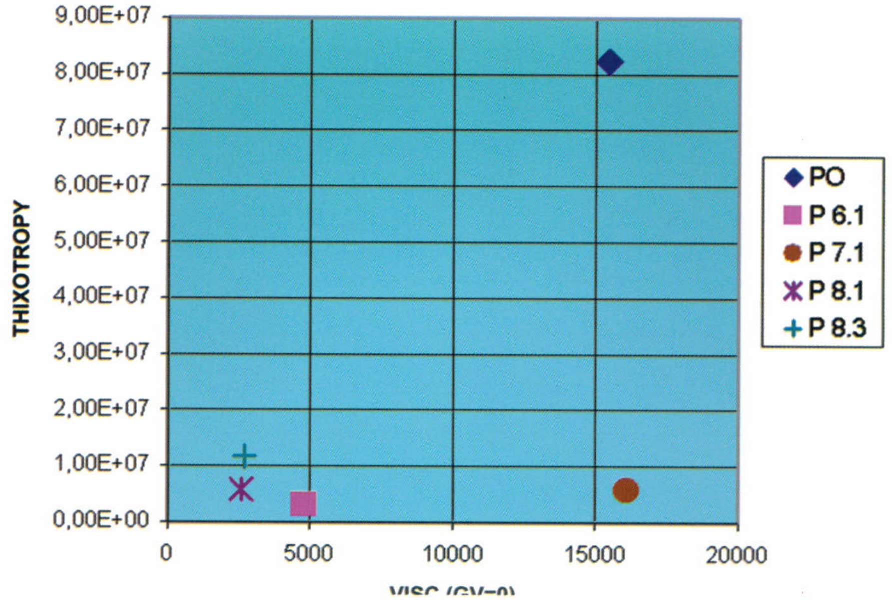


Figure 11. Thixotropy versus maximum viscosity at low shear rates.

4. CONCLUSIONS

- In order to apply a glaze by rotogravure, it is necessary to bear in mind that the variables of the machine (deck speed, blade attack angle, etc.) will only provide more or less grammage on the tile; the proper application of the glaze layer depends particularly on the rheological conditions of the glaze itself and the conditions of the production line.

- It is obvious that the application conditions in the different types of products (single firing, double firing, porcelain tile, etc.) will differ from each other.
- The three fundamental variables that influence this type of application are:

  - drying time of the glaze layer: the longer this is, the better will the final finish be. At lower body temperature, smaller water content of the suspension and a greater degree of deflocculation, drying time will be longer.

  - thixotropy and viscosity at low shear rates: the lower, the better the final finish. These parameters can be adjusted by the nature of the applied glaze and the type of vehicle used to condition it for the rotogravure application technique.

  - glaze melt viscosity during the firing: the higher this is, the worse the results will be.

- For suitable stability of the prepared glaze it is indispensable to have a minimum of 9-10% vehicle relative to the weight of liquid glaze. This will avoid problems of sedimentation, "dry-up" of the glaze in the machine, unsteady pumping and insufficient flow rate in proportioning, etc.
- The transparent glazes will not have the same ease of application as the white or matt glazes, since transparent glazes are more difficult to apply, as may be observed in the rheological values of Figures 8 and 9.
- A short but intense milling or stirring of the conditioned glaze will improve the rheological conditions and therefore glaze application.

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