DEVELOPMENT OF CERAMIC TILE DECORATION BY FOUR-COLOUR ROTOGRAVURE PRINTING. APPLICATION OF THE KRIEGER-DOUGHERTY MODEL

[(1)] A.Torres, [(1)] J. A. Tirado, [(1)] M. A. Babiloni, [(2)] F. Lucas, [(2)] J. Albalat, [(3)] E. Bou, [(3)] A. Saburit, [(3)] M. J. Orts, [(3)] Y. Bautista

[(1)] SYSTEM ESPAÑA, S.A. Castellón. Spain

[(2)] FRITTA, S.L. Onda, Castellón. Spain

[(3)] Instituto de Tecnología Cerámica (ITC)

Asociación de Investigación de las Industrias Cerámicas (AICE)

Universitat Jaume I. Castellón. Spain

ABSTRACT

Decoration by four-colour rotogravure printing has not become widespread due to a series of problems that have been analysed in the present study. This analysis has allowed a work system to be developed that enables this decoration to be carried out.

This type of decoration requires high machine-cylinder-incision precision in order to avoid so-called 'moiré' effects (inappropriate alignment of the printed dots). High colour consistency is also required, which depends on a large number of variables: properties of the glaze compositions, characteristics of the silicone roller, duration of the incision, ink properties, application conditions, etc.

The study conducted was divided into three parts. In the first, the most appropriate roller characteristics (type of silicone and incision) were selected

with a view to obtaining optimum resolution and stability during production. In the second, the inks were developed, the most appropriate vehicle, base, and ceramic pigments being selected. In the third, the results were validated in a semi-industrial line, using rotogravure machines with automatic temperature, viscosity, and density adjustment.

The ink components were specifically selected to obtain stable suspensions with regard to the appearance of minor colour differences, sedimentation, printed dot definition, and blade and cylinder wear.

Since correct rotogravure application requires a certain ink viscosity, which will largely depend on the vehicle used, it was decided to use the Krieger-Dougherty equation to predict the variation in ink viscosity with solids content as a function of the type of vehicle used.

The results of the present study have enabled a work methodology to be established that allows ceramic tile decoration by four-colour rotogravure printing.

1. INTRODUCTION

The rotogravure technique is used in ceramic tile decoration, and enables designs to be printed on flat surfaces at high speed. In this printing process, numerous variables influence the end decoration, as different studies have shown [1][2][3][4][5].

The development of four-colour rotogravure printing decoration would allow the development of the designs to be simplified, since it makes it possible to apply colour management programs, as well as to reduce colour stocks and, generally, to simplify the decoration process [6].

In order to carry out decoration satisfactorily by four-colour rotogravure printing a series of requirements must be observed: high machine-cylinder-incision precision, with a view to avoiding the 'moiré' effects (inappropriate alignment of the printed dots) and high colour consistency, i.e. stability in the quantity of deposited ink, which depends on numerous variables, such as glaze layer characteristics, ink properties, and application conditions.

The objective of the present study was to select the type of silicone-incision combination that provided the best printing resolution and absence of defects, and also to develop inks for four-colour printing that ensured high colour stability in the decoration.

The development of four-colour printing inks needed take into account two features: the selection of the solids and the selection of the vehicle. The solids, i.e. the pigment and flux, define the colour of the decoration, while the vehicle defines the rheological behaviour of the ink, which influences printed dot definition.

The application of the Krieger-Dougherty model enables the dependence of viscosity on the solids concentration to be predicted, so that the number of tests needed to characterise a new formulation can be considerably reduced when a new vehicle or a different solid (change of base or pigment) is used [7][8].

On the other hand, as might be expected, the solids content in an ink composition notably influences its colour development. This fact may be essentially attributed to the variation in pigment concentration [9].

The combination, between the relationship predicted by Krieger-Dougherty and that established between the solids content and the colour obtained in each ink, will determine the optimum ink preparation conditions.

Ceramic tile decoration by four-colour printing has been achieved through the development of ink-jet printing; this technique displays a series of disadvantages, however, such as lower colour intensity in the decoration, need to develop specific materials that match the demands resulting from the use of printing heads, and lower printing speed.

2. DEFINITION OF ROLLER CHARACTERISTICS

Different types of silicones and incisions can be used in roller preparation. It is necessary to identify the most suitable type of silicone and incision to obtain the best possible dot definition.

2.1. Experimental.

In the context of an existing silicone format in the market, together with the most appropriate laser configuration for the silicones, a series of tests were conducted with a view to obtaining an appropriate combination of silicone and incision, for suitable decoration work on a glazed substrate.

The tests consisted of a number of adjustments of the various laser incision parameters applied to different silicone surfaces. Scales of grey were obtained, the result of the silicone engraving being evaluated, as well as the result of the use of this silicone in rotary rotogravure printing, for which a videoscope was used.

The initial printing checks of the incision adjustments were conducted with a standard black ink on paper. The ink composition was as follows:

- 50% glossy base.
- 50% black colouring oxide.
- Rotogravure vehicle (solids content = 50% by weight).
- Draining time of 26 seconds in a Ford no. 4 cup.
- DIN A3 paper with a weight of 20 g.

With regard to the application conditions of the rotary machine, the standard conditions for the company machine involved were applied:

- Conveyor belt speed = 30 m/min.
- Cylinder-tile pressure = - 2 mm.
- Cylinder slide = 0,7%.
- Double-edge blade holder with one 0,15-mm-thick stainless steel blade.
- Scraper height = 230 (cylinder 720) and 335 (cylinder 1440).
- Blade-cylinder weight = -2.

The image used to develop the appropriate silicone-incision combination was based on the following grey scale and three designs:

Based on the engraving on different types from silicones, using different types of incisions, the printing on paper and photographic visualisation of both the printing and videoscopic observation of the incised cavities, the suitability of the silicone-incision combination was determined for correct deposition or printing of the ink for appropriate work in developing earthenware wall tile models by four-colour printing.

Table 1 details the nomenclature used in this part of the work, as well as the references of the examples relating to the photographs shown in the results section.

SILICONE	INCISION	Level of grey scale		
		10%	50%	90%
S1 / S2/ S3	I1	Ej: S1-I1	Ej: S2-I1	Ej: S3-I1
S1 / S2/ S3	I2	Ej: S1-I2	Ej: S3-I2	Ej: S2-I2
S1 / S2/ S3	I3	Ej: S2-I3	Ej: S3-I3	Ej: S1-I3
S1 / S2/ S3	I4	Ej: S3-I4	Ej: S1-I4	Ej: S2-I4

Table 1. Nomenclature used.

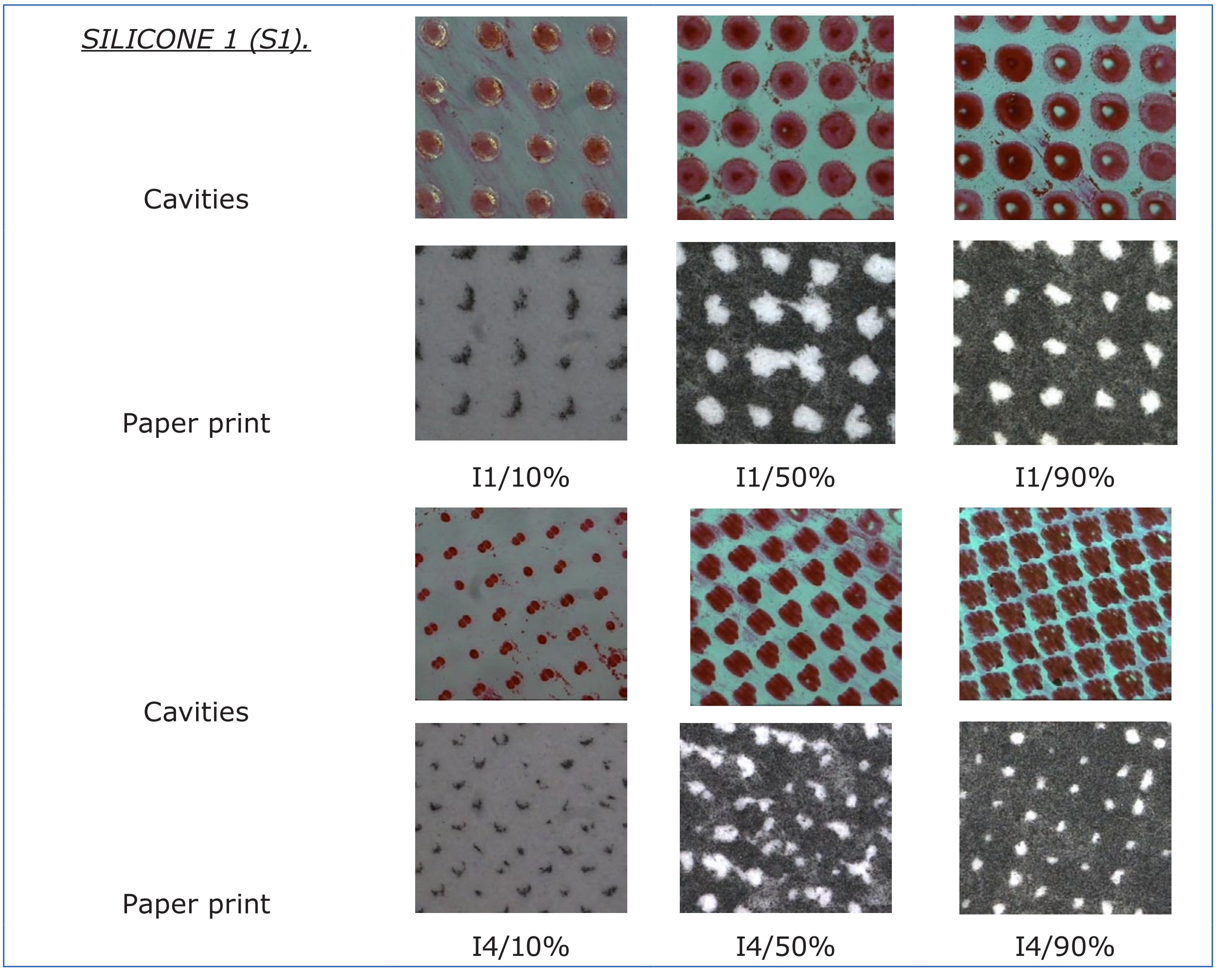
The results were used to determine the most appropriate incision and type of silicone, in order to be able to obtain optimum, reliable results in carrying out appropriate and stable production work in the ceramic tile manufacturing process.

2.2. Results.

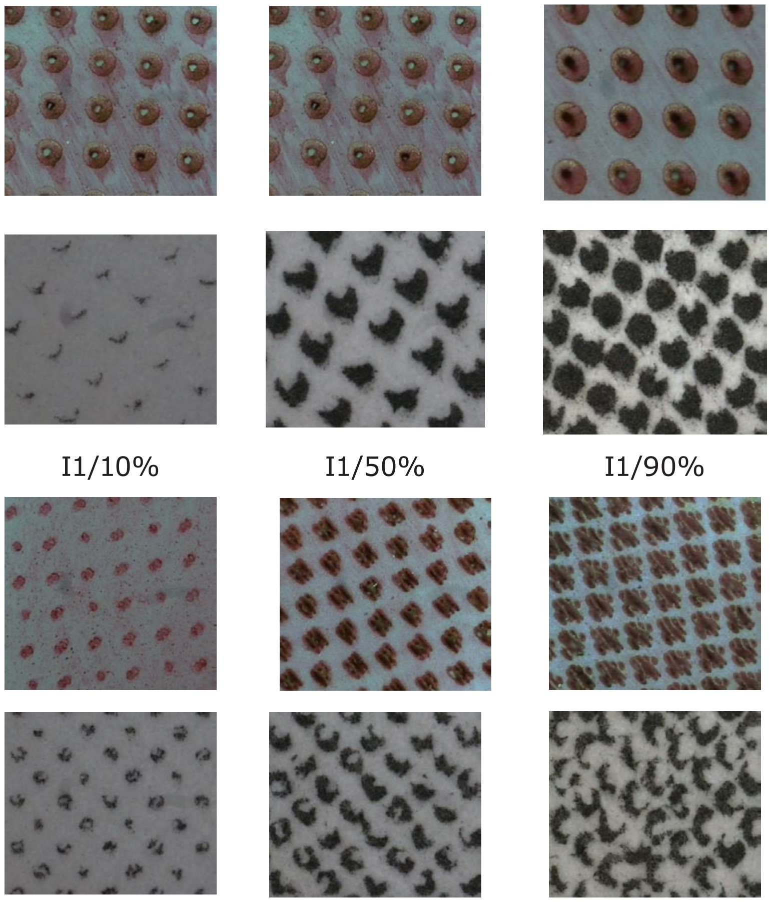
2.2.1. Development of the appropriate silicone-incision combination.

The different photographs taken with the videoscope, relating to the cavities obtained in each of the tests, were then visualised. The cavities incised in the silicone and the results of the printing on paper were examined. For the sake of simplicity, the results are only shown for two silicones and two incisions.

The photographs show that the visual appearance of the cavities differs considerably from the visual appearance of the prints. Logically, the most consistent and real conclusions will be those drawn from efficient production outcomes; nevertheless, this method enables key features to be determined.



SILICONE 3 (S3).



Cavities

Paper print

I1/10% I1/50% I1/90%

Cavities

Paper print

I4/10% I4/50% I4/90%

In the first place, it is obvious that though silicone S3 provides interesting printing results regarding dot definition, it may be said that printing dot gain is low. This could be caused by the elasticity of the silicone, which offers little resistance to the travel of the cylinder levelling blade, which, together with the shallowness of the cavities, facilitates draining from inside the cavities, with the ensuing reduction in the quantity of ink deposited on the surface.

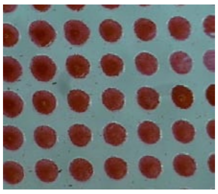
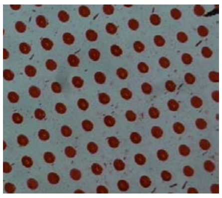
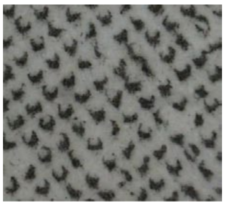
Secondly, by way of comparison with silicone 3, the results can be visualised for silicone 1 which, though they resemble each other with regard to the cavity and the print, appear to provide better results as regards stable geometric cavity shape in all the proposed incisions in relation to S3.

Logically, at this point it appeared obvious to establish a consistent dot, in the choice of silicone: in this case, this meant choosing silicone 1. This is because, while the discharged quantity (which solely entailed greater colour intensity) can readily be offset by optimising the relationship between the base and the colouring oxide of each ink, the perfection of the cavity is fixed. As a result, if the photographs are examined, silicone 1 is observed to offer better results in relation to the geometric shape of the cavity than silicone 3, possibly owing to the elastic characteristics of the respective silicones.

On the other hand, as far as the selection of the most suitable incision was concerned, of the four tested incisions, the one that visually displayed the best prospects for production work was incision 1 (I1); however, it was observed that the number of dots by unit surface area was relatively low, as a result of which the incision was optimised.

2.2.2. Optimisation of the silicone-incision choice. Silicone (S1)+Incision 5 (I5).

Using the same I1 incision concept, the printing resolution was enhanced, providing the images with a greater graphic quality. In the following figures, an improvement in regard to printing resolution can be observed, while holding the quality in the geometric aspect of the cavities.

SILICONE 1 (S1).		
Cavities	 Incision 1 (I1)	 Incision 5 (I5)
Paper print	 Incision 1 (I1)	 Incision 5 (I5)

3. DEVELOPMENT OF INKS

Ceramic tile decoration by rotogravure is a very widespread process, though it has not evolved towards four-colour printing, among other reasons, because of the absence of ceramic inks that remain stable with time during production. The present study has addressed that variable as a fundamental objective, and the development has been carried out by focusing on the following physical variables of the inks:

- Colorimetric aspects:
  - Obtainment of an ink palette that, by superposition, provides a broad colour palette, matching ceramic production needs.
- Integration with glaze compositions:
  - Four-colour printing decoration entails the superposition of inks in order to obtain the desired colours, which is why it is important to obtain inks that integrate appropriately with the glaze compositions without producing high- or low-relief effects, including in areas with four superimposed inks.

- Rheology:
  - Ink viscosity and surface tension need to be adjusted for appropriate performance in the decoration process:
    - Roller charging and discharging.
    - Dot gain (definition).
    - Maintenance of the suspension (without sedimentation).
- Colour stability during production:
  - Variations in colour stemming from the ink are caused by:
  - Variations in ink density during production (variations in solids content).
  - Variations in ink colour percentage (variations in the pigment/fluxing base ratio).

3.1. Selection of ink components.

In order to carry out this process, the following were studied:

- Calcined colours.
- Micronised ceramic fluxes.
- Plasticisers.
- Modifiers of rheological characteristics.
- Vehicles.

Calcined colours

Numerous tests were conducted and it was decided to work with a basic palette of:

- C: Cyan (slightly greenish blue).
- M: Magenta (reddish brown).
- A: Yellow.
- N: Black.

The resulting palette is much broader than in the case of decoration by digital jet printing. In rotogravure decoration, there is no constraint regarding the small particle size that needs to be used in digital jet printing, and livelier colours are thus obtained, with a richer colour range.

Ceramic fluxes

Each ink was adjusted such that fusibility was appropriate in order to obtain:

- Perfect integration with the glaze compositions (including in the case of the superposition of several inks).
- Optimum colour development, with fluxes that highlighted the pigment colour.
- The fluxes used were based on micronised crystalline borate frits with specific fusibilities for each ink.

Plasticisers

Plasticisers serve to obtain optimum ink rheological characteristics, as well as to maintain the suspension. The following issues were considered:

- Ink uniformity.
- Non-separation of liquid and solid phases, contributing to colour stability during production.
- Appropriate viscosity and surface tension.

Modifiers of rheological characteristics

In addition to plasticisers, it was necessary to use viscosity and surface tension modifiers. Each colour has a different behaviour, which needs to be adjusted.

Vehicles

In order to choose the vehicle, the Krieger-Dougherty model was applied, which is described greater depth in the following section. The vehicle that provided the most satisfactory results was V1.

Ink preparation

For appropriate homogenisation of all products, a batch microbead mill was used. Milling time was 40 min for a 5-kg ink charge.

3.2. Application of the Krieger-Dougherty model in ink development.

The application of the Krieger-Dougherty model allows the dependence of viscosity on the solids concentration to be predicted, so that the number of tests needed to characterise a new formulation can be considerably reduced by using a new vehicle or another solid (change of the base or pigment) [8]. The equation of the Krieger-Dougherty model is as follows.

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

Equation 1.

where ηr is the relative viscosity of the ink in relation to that of the vehicle

($\eta\infty$ ink/$\eta\infty$ vehicle), φ and φm are the volumetric content and the maximum packing fraction, respectively, and [η] is intrinsic viscosity.

The variation of the ink solids charge does not only affect suspension rheological behaviour. Another important parameter affected by this variation is the colour strength that the applied and fired inks develop. As is well known, the greater the ink solids content, the greater is their pigment concentration and, hence, the resulting colour intensity [9]. For this reason, in the present study, the variation in colour with solids volume content was also simultaneously determined.

3.2.1. Experimental.

Materials

The study was conducted using two vehicles (V1 and V2), a base designated B, and the four pigments selected in the previous section (A, C, M, and N).

Ink preparation

The quantity of pigment used in every case was 30% by weight in relation to the total solids. To determine the volumetric content (φ) of the suspension it was necessary, first, to determine the true densities of the base and of the pigments with a helium stereopycnometer.

Determination of the curve $\eta r=f(\varphi)$

The rheological parameters of the inks were measured in a rheometer, controlling the applied shear stress and measuring the resulting strain at each moment. During the test, the sample was kept thermostatted at the test temperature (35 ºC).

The measurements were made using a system of concentric cylinders. The flow curve and the viscosity curve were obtained by flow tests in which the shear stress was controlled.

The $\eta r=f(\varphi)$ curve was calculated in all cases in the high-shear region. This was done by determining $\eta\infty$, fitting the flow curves of each sample to the Sisko model, except the flow curves of the vehicles with no solids charge, which were fitted to the Newton model.

Sisko: $\eta = \eta_\infty + \mathbf{k}\left(1/\dot{\gamma}\right)^{\mathbf{m}}$ Newton: $\sigma = \eta \cdot \dot{\gamma}$

where η is viscosity for a certain shear rate, $\eta\infty$ is viscosity at high shear rates, $\dot{\gamma}$ is the shear rate, and k and m are the constants of the Sisko model.

Determination of colour variation with solids volume content

The ink suspensions were applied on to an unfired, glazed, white-firing earthenware wall tile body, using an applicator with an opening of about 60 µm. The test pieces with the application were fired in electric laboratory kiln, using a thermal cycle with a heating rate of 25ºC/min to a peak temperature of 1120ºC, with a six-minute dwell at that temperature.

The chromatic coordinates of the resulting fired glazes were measured with a diffuse reflectance spectrophotometer. The measurement conditions of the instrument consisted of a standard CIE D65 illuminant and standard CIE observer at 10º. The measurements were made using the CIELab system of chromatic coordinates. In order to determine the colour variation, the parameter ΔE* was used, taking a tile without an ink application as a references for this purpose. The value of ΔE* obtained was thus related to the degree of colour saturation in each ink.

3.2.2. Results.

The results obtained from the fit of the Krieger-Dougherty model for the inks prepared with vehicle V1, base B, and each of the pigments A, C, M, and N are set out below.

In order to obtain these results, flow curves were plotted of the inks prepared at different solids contents, determining the viscosity at high shear rates from the fits to the Sisko model. Figure 1 depicts the evolution of relative viscosity as a function of solids volume content, the experimental data being plotted as points and the fits to the Krieger-Dougherty model being plotted as solid lines. The figure shows how the behaviour differs, depending on the pigment used, and how the use of the model satisfactorily fits the experimental data.

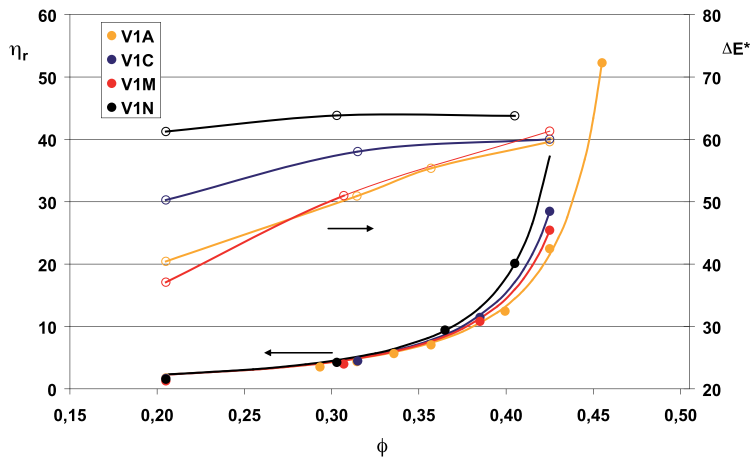


Figure 1. Variation of relative viscosity and ΔE with solids volume content for the inks V1A, V1C, V1M y V1N.*

Figure 1 also shows the evolution of ink colour development with solids content. In the four colours, the colour intensity increases when the solids content increases, the darkest inks (V1N and V1C) being the ones that stabilised colour by saturation earliest. These results indicate that inks V1A and V1M will be the ones that give rise to more problems in relation to colour changes, owing to the variation in ink solids content (density variations).

When the Krieger-Dougherty model was applied, the vehicle-pigment interaction and the sphere-geometry of the particles were assumed to be the same for all test pigments: it was therefore assumed that the intrinsic viscosity ($[\eta]$) was the same in all the inks prepared with vehicle V1.

The values of the maximum packing fraction (φ_m) for each of the inks and the intrinsic viscosity ($[\eta]$) obtained in the fit of the model are given in table 2. The table shows that ink V 1N displays the smallest maximum packing, which means that, for a given volume content, this ink has the highest viscosity.

The values obtained in the calculation of the intrinsic viscosity and the maximum packing fraction, using the Krieger-Dougherty model and starting with the empirical data of the suspension viscosities, are consistent with the results obtained in other studies [10]. The calculated intrinsic viscosity value, compared with the results found in the literature, lies between the values corresponding to submicrometric spheres and spheres of 40 µm. Observation in an electron microscope of pigment particles shows how, in the four cases, these display a sphere-like geometry.

In the case of the maximum packing fraction, apart from the geometric shape of particles, the value is also related to the average size and bimodal character of the solid particle size distribution [9]. These results match those predicted by the Farris model [11].

Ink	V1A	V1C	V1M	V1N
φ_m maximum packing fraction	0.487	0.469	0.475	0.458
$[\eta]$ intrinsic viscosity	3.164	3.164	3.164	3.164

Table 2. Maximum packing fraction and intrinsic viscosity used in the fit of the Krieger-Dougherty model.

Once the behaviour of the inks prepared with each of the studied pigments and the V1 vehicle had been determined, it was possible to predict the behaviour of other inks prepared with these pigments in the same base-pigment ratio with other different vehicles.

In order to verify this assumption, a rheological study was conducted of an ink prepared with pigment A, base B, and vehicle V2 (V2A). In this case, only four different solids contents were tested in comparison with the nine that were needed to characterise ink V1A properly. In order to determine the parameters of the

Krieger-Dougherty model for this ink, the maximum packing fraction was assumed to be same as that of ink V1A, since the same solid was used in both inks.

Figure 2 shows a plot of the evolution of relative viscosity as a function of the solids volume content for inks V1A, V2A, and V1N. In this case, the figure shows that the fit with the Krieger-Dougherty model (solid lines) also appropriately reproduces the experimental data (points). It also shows that, for a given solids content, the use of the V2 vehicle gives rise to an ink with a higher relative viscosity than that with the V1 vehicle, and is more similar to that of ink V1N which, as remarked previously, has a higher relative viscosity owing to its lower maximum packing fraction.

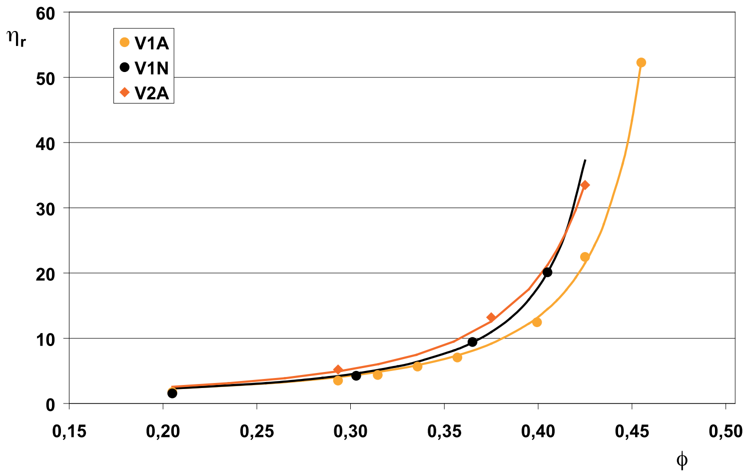


Figure 2. Variation of relative viscosity with solids volume content for inks V1A, V1N, and V2A.

Ink	V1A	V2A
Solids content (%)	55.0	59.9
φ (%)	0.31	0.35
$\eta_{\infty\ ink}$ (mPa·s)	**152**	**152**
$\eta_{\infty\ vehicle}$ (mPa·s)	31.6	15.8
η_r	4.8	9.6

Table 3. Rheological characteristics for the samples with vehicles V1 and V2.

Using the ink viscosity required by the application system, the solids content can be determined in the conditions under which the ink must be prepared. Table 3 presents an example. Assuming a viscosity of 152 cP is needed at high shear rates, the solids volume content can be calculated at which the inks need to be prepared when the two tested vehicles V1 and V2 are used.

Using vehicle V2 enables higher solids contents to be reached, which is beneficial, because higher colour intensities would result; however, it must be taken into account that in the work area (φ=0,35 %), vehicle V2 gives rise to higher variations in viscosity with solids content, making the ink less stable with regard to the appearance of the colours.

4. VALIDATION OF THE RESULTS ON AN INDUSTRIAL SCALE

Several trials were conducted on a semi-industrial level in the Fritta pilot plant to verify the results obtained. The trials were performed under very similar working conditions to those used in industrial production:

- Unfired porous single-fire white-firing earthenware tile body and an unfired porcelain tile body.
- Tile temperature during glazing: 90 – 100 ºC.
- Wetting with an airless gun: 4 g on 30 x 30 cm.
- Engobe application by bell waterfall: 35 g on 30 x 30 cm.
- Glaze application (gloss or matt) 70 g on 30 x 30 cm.
- Decoration of the pieces with a Rotocolor S-5 four-colour printing machine, using two types of inks:
    - Cyan – Magenta – Yellow – Black (CMYK).
    - Cyan – Magenta – Beige – Black (CMBK).
- The palettes obtained were recorded in photoshop using a palette of profiles that was subsequently used for the development of models.
- The tiles were fired in a roller kiln in industrial cycles.

Some of the pieces obtained are displayed below, which show a broad colour range, as well as the integration and definition of the inks in both the glossy and matt glazes.

Gloss (CMYK)

Gloss (CMBK)

Matt (CMBK)

Figure 3.

5. CONCLUSIONS

The following results were obtained in the study:

- A type of incision has been developed for rotogravure that facilitates the work in four-colour printing, in which the duration of this type of incision is the same as that of a standard incision.
- A range of inks have been developed that yield a very wide range of colours.
- The combination of incision and inks provide great colour stability over time during the production work.
- Small differences in centring do not affect the aesthetic result of the pieces.
- The same inks can be used to produce models with a very different graphic appearance.
- The development of graphic ceramic projects is simplified by the use of colour management systems.

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