RATIONAL METHOD FOR SCREEN-PRINTING INK PREPARATION AND ADJUSTMENT

V. Martí(*), P. Notari(*), J. Portolés(*), S. Rodríguez(*), C. Felíu(**), V. Sanz(**), G. Mallol(**), M. Monzó(**)

(*)TAULELL, S.A.
(**)Instituto de Tecnología Cerámica (ITC)
Asociación de Investigación de las Industrias Cerámicas (AICE)
Universitat Jaume I. Castellón. Spain.

1. INTRODUCTION

In ceramic tile manufacturing it would be desirable for all the lots of a given model to have exactly the same colour[1, 2]. However, the variations in the characteristics of the materials and operating conditions used make this hard to achieve.

On putting a model into production, one of the prime objectives is precisely that of matching the reference colours. Although there may be different reasons for shades (minor colour differences) to arise, colour is often adjusted by modifying the screen-printing inks.

The following steps are usually involved in ink preparation[3] (Fig. 1):

- Proportioning the different constituents in the amounts specified in the formulas.
- Mixing the solids with the vehicle to obtain a homogeneous suspension.
- Ink refining. This is to reduce particle and aggregate size to enhance ink behaviour.

[1]. NEGRE, F.; MORENO, A.; SÁNCHEZ, E., et al. *Factores que influyen sobre la variabilidad de la tonalidad de baldosas cerámicas.* Ponencia presentada al XXXIV Congreso Anual de la Sociedad Española de Ceramica y Vidrio. L'Alcora (Castellón), 14-17 September, 1994. (Unpublished)

[2]. MARTÍ, V.; PEÑALVER, J.; PORTOLÉS, J., et al. *Study of screen-printing application control variables and their influence on shades in tiles.* In: IV World Congress on Ceramic Tile Quality (Qualicer). Castellón, 1996.

[3]. SÁNCHEZ, E.; SANZ, V.; NEGRE, F., et al. *Assessment of shades in screen-printing inks.* In: IV World Congress on Ceramic Tile Quality (Qualicer). Castellón, 1996.

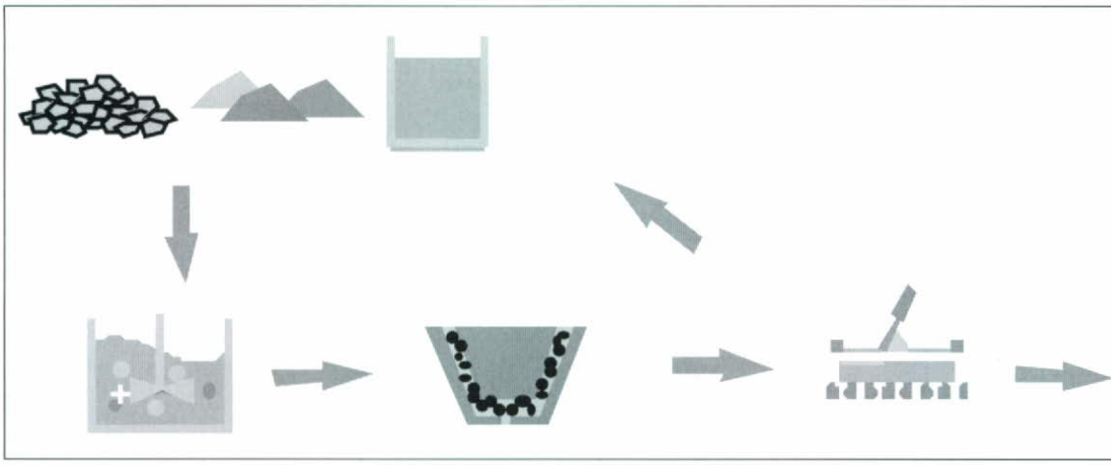

Figure 1. Current screen-printing ink preparation method.

After preparing the ink by the previous steps, it is necessary to verify whether the ink exhibits the expected behaviour and characteristics under actual operating conditions, otherwise adjustments need to be made.

Vehicle additions can easily be performed, since the vehicle blends readily with the ink. However, solids additions, usually with a view to correcting colour, require repeating the whole preparation process to obtain suitable solids dispersion. In both cases, the results are always checked prior to putting the model into production.

Besides the additional work that such corrections involve, it must also be taken into account that they affect the ink preparation rate, owing to the downtime involved in the checks. This is detrimental to process flexibility and requires anticipating ink needs with sufficient time in advance.

In spite of the importance of the number of corrections made before obtaining the targeted ink, such adjustments are usually performed empirically, requiring an number of trials.

On the other hand, ink adjustments while the models are being developed are also made by entirely empirical methods, which increases the work required to obtain the sought-after ink.

The present study demonstrates the efficiency of rational colour matching methods in preparing and adjusting screen-printing inks, and sets out some practical consequences stemming from the use of such methods.

1.1. COLOUR MATCHING THEORIES

The attributes of an object's appearance are related to the way in which the object modifies the light that strikes it[4]. The four main processes arising when light strikes a non-metallic object (Fig. 2), are as follows:

[4]. MESTRE, S. *Compuestos del sistema Fe_2O_3-Cr_2O_3, estudio cinético y colorimétrico.* Castelló: Universitat Jaume I, 1997. (Doctoral dissertation).

- Specular reflection at the object's first surface (associated with gloss).
- Scatter in the material, related to diffuse reflection.
- Absorption in the material (main cause of colour).
- Regular transmission through the object if the material is more or less transparent.

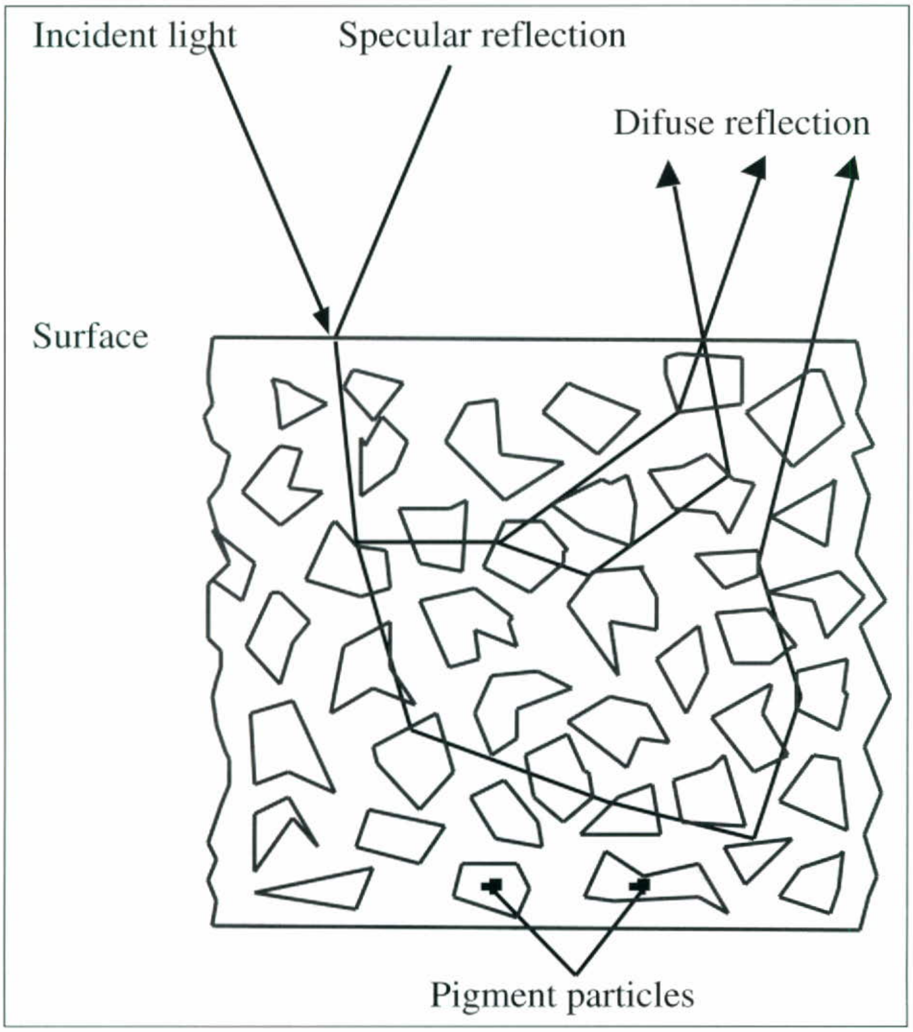

Figure 2. *Interaction of light with pigmented objects.*

The Kubelka-Munk theory[5] simplifies the above processes and establishes that materials partially absorb the light that they receive while the rest is scattered. The proportion of absorbed light depends on the material's coefficient of absorption (K), whereas dispersed light depends on the material's scatter factor (S). Moreover, the background onto which the sample under observation is set (if it is transparent or translucent) and the thickness of the sample also affect parameters K and S.

[5]. SHAH, H.S.; GANDHI, R.S. *Medida e igualación del color en textiles*. Valencia: IMPIVA, 1993.

If the background effect can be obviated, the equations derived by Kubelka and Munk yield the following relation between reflected light and the coefficients of absorption (K) and scatter (S):

$$R = 1 + \left(\frac{K}{S}\right) - \left[\left(\frac{K}{S}\right)^2 + 2\left(\frac{K}{S}\right)\right]^{\frac{1}{2}} \quad (1)$$

Or inversely:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (2)$$

As for a given pigment, the quotient K/S has a linear relationship with pigment concentration (which does not hold for reflectance), using the quotient enormously facilitates resolving colour matching problems.

Thus, on establishing this linear relationship, the assumption can be made that the relation between the coefficients of absorption and scatter of pigment mixtures $(K/S)_M$ can be estimated by applying the linear mixtures law, that is:

$$\left(\frac{K}{S}\right)_M = c_1\left(\frac{k}{s}\right)_1 + c_2\left(\frac{k}{s}\right)_2 + \ldots + \left(\frac{K}{S}\right)_b \quad (3)$$

where c_i represents the proportion of each pigment used in the mixture, $(k/s)_i$ represents the relation between the individual coefficients of each pigment, and $(K/S)_b$ represents the behaviour of the non-pigmented base.

The above equation holds for each wavelength. Therefore, if the reflectance curve of the individual pigments is determined, the relation $(k/s)_i$ can be computed at each wavelength for each pigment, and the mixture's reflectance can then be calculated by means of the above equation.

It is sometimes necessary to compare the colour matching result by employing specific chromatic coordinates, which can readily be done from the resulting reflectance curve, using suitable transformation equations.

2. OBJECTIVES

The objectives of the study were as follows:

- Definition of a screen-printing ink reproduction and adjustment technique based on an objective, quantifiable method that allowed carrying out these tasks more efficiently.

- Proposal of a rational methodology for screen-printing ink preparation, allowing better management of the materials used, as well as improving the flexibility and productivity of the screen-printing ink preparation stage.

3. METHODOLOGY

Each pigment's colour was characterised on making up the inks with the respective pigment and frit concentrations specified in each case. The inks were all prepared at a solids content of 55% (kg solid/100 kg total weight).

The resulting inks were applied to unfired glazed tiles by means of a printing screen with a mesh count of 77 and 100% ink release.

The test specimens were fired in an electric laboratory kiln at a peak temperature of 1100 °C for 3 minutes, using a heat-treatment schedule with a heating rate of 25 °C/min.

The colorimetric attributes of the fired test specimens were determined in a diffuse reflectance spectrophotometer.

The study was conducted using the CIELab colorimetric scale, whose parameters are defined as follows:

L^* indicates the position on the white axis ($L^* = 100$), black ($L^* = 0$).

a^* indicates the position on the red axis ($a^* > 0$), green ($a^* < 0$).

b^* indicates the position on the yellow axis ($b^* > 0$), blue ($b^* < 0$).

In this system, the difference in colour between two specimens is given by the modulus of the vector that joins the points of the two specimens' colour space. The modulus is designated ΔE^*.

Generally speaking, colours that differ by less than 0.5 units in ΔE^* are not perceivable by the average human observer, though for colours very close to white, the distinguishing threshold appears to be slightly lower.

4. CURRENT COLORIMETRIC SPACE

Before determining a suitable working method, it was considered convenient to identify the colorimetric space region in which the current screen-printing inks lay.

On considering total pigment consumption in recent months, it was found that a group of 17 pigments made up 94% of total pigment consumption.

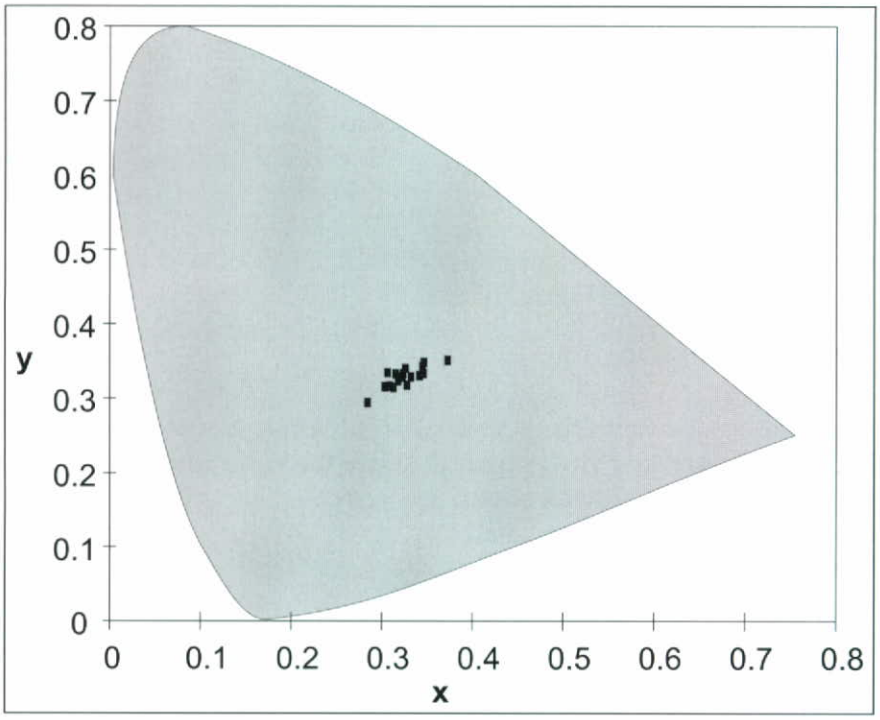

Figure 3. *Situation of the tested ink coordinates in the colour space.*

The exclusive use of these pigments would involve a drop of around 40% in the total number of pigments used.

The colour space region in which the most common inks lay was defined by this group of pigments. Logically, there might be some minor colours that could not be reproduced by blending pigments from this group, however, owing to scarce use, this did not warrant changing the approach.

With a view to graphically illustrating the colorimetric space used, Fig. 3 depicts the x and y coordinates of the 17 selected pigments. These coordinates were chosen because they present the colorimetric space within which the colours that can be perceived by the human eye are delimited (dark area).

It can be observed that the colour field exhibited by the tiles (centre points in the graph of Fig. 3) is relatively small, if this is compared with the entire visible colour space.

Ceramic pigments yield colours that are much stronger than the ones found in the region indicated in the above graph, however, the decorative use to which the tiles involved are put tends to require soft colours.

5. RESULTS

5.1. VALIDITY OF INK COLOUR MATCHING

One of the main issues involved in achieving the objectives set in this study was being able to accurately model the behaviour of the ceramic pigment mixtures and resulting colours, so that pigment characteristics would allow predicting with sufficient accuracy the colour that mixtures of pigments would exhibit, on application by screen printing to ceramic tiles.

Colour matching techniques can basically been divided into two groups: spectrophotometric techniques and colorimetric techniques. Common to both techniques is the fact that to reproduce a colour, the colour's colorimetric attributes need to be determined beforehand, as do certain other characteristics (depending on the method employed) of the pigments to be used in reproducing the colour. Both methods are generally based on the Kubelka-Munk theory.

The spectrophotometric techniques, as their name indicates, are designed to reproduce the reflectance curve of the colour to be matched. This is done by using numerical calculation methods that attempt to minimise the differences between the reflectance curve to be reproduced, and the one obtained by mixing the pigments. As the matching calculation used in this technique does not directly take into account the effect of the type of light used, it predicts formulas whose results are virtually independent of the type of lighting under which the outcome will later be examined (i.e. the formulas are not metameric). Thus the formulas predicted by this method do not usually reproduce the colours accurately.

However, the colorimetric methods that attempt to match the colorimetric cooordinates of the sample to be reproduced, as they account for the lighting used on computing these coordinates, as well as the observation conditions employed, tend to yield more accurate results, though they may exhibit greater metamerism.

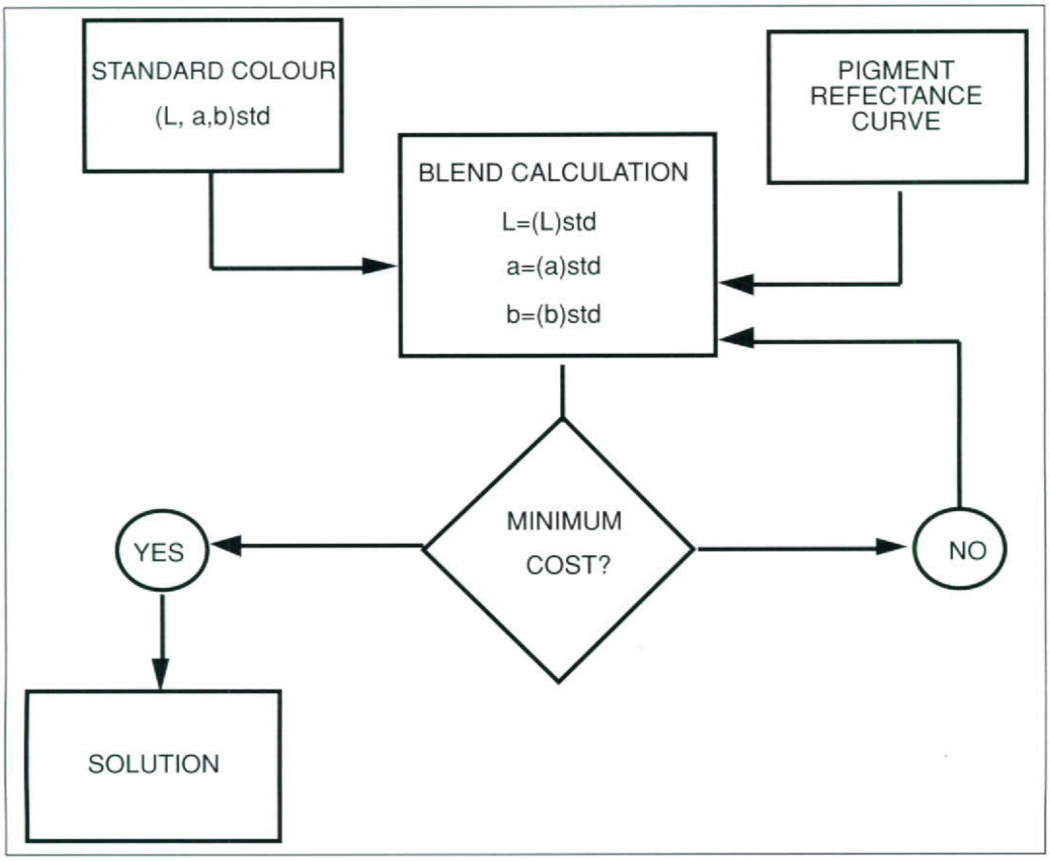

Figure 4. Flow chart of the screen-printing ink matching and adjustment method.

In attempting to establish an accurate colour matching procedure, considering that the mixtures did not usually exhibit any great degree of metamerism owing to the relatively small number of pigments involved (compared to other branches of industry), it was decided to develop a colorimetric colour matching technique based on the Kubelka-Munk theory.

Industrial colour matching goes beyond the pure calculation entailed in reproducing a given colour using various pigments, as amongst the multiple possible solutions only a few might be economically of interest. Indeed, this would at times be the prime reason for needing to reproduce a colour from certain pigments.

Fig. 4 depicts the flow chart of the procedure developed for matching and adjusting colour, which includes the possibility of formulating economically optimised inks.

With a view to confirming the possibility of reproducing screen-printing ink colours by the above theory, two industrial inks were reproduced by combining a limited number of pigments exhibiting colorimetrically very different characteristics.

5.1.1. REPRODUCTION OF A BEIGE SCREEN PRINT

This section sets out the reproduction of a beige ink used in industry, which is obtained from a single pigment.

The pigments used in reproducing this ink were a red, a blue and a yellow pigment, with which inks were prepared at the same concentration as the reference ink. Subsequent mixing of these inks then yielded the various tested compositions.

Table 1 details the reference beige ink composition, as well as the compositions of the screen-printing inks used to reproduce it. The chromatic coordinates of these inks are also listed, and it can be observed that the pigments employed in reproduction were quite different from the targeted colour.

	Composition					Colour			
Ink	Frit	Pigment				L*	a*	b*	ΔE*
		Beige	Red	Blue	Yellow				
Beige	91.9	8.1				83.2	-0.4	8.3	
Red	91.9		8.1			81.5	4.9	9.2	
Blue	91.9			8.1		67.9	-2.5	-12.8	
Yellow	91.9				8.1	88.2	-5.3	14.5	
B1	91.9		3.5		4.5	84.9	0.3	11.0	3.2
B2	91.9		3.9	0.6	3.6	83.0	0.1	8.5	0.5
B3	91.9		3.4	0.7	4.0	82.9	-0.5	8.0	0.5

Table 1. *Composition and chromatic coordinates of the inks used in reproducing a beige ink.*

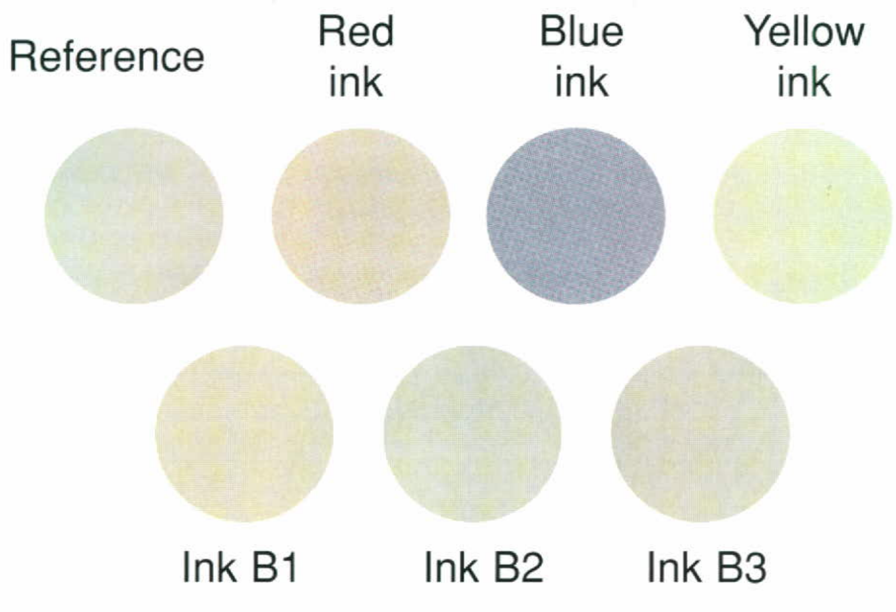

Figure 5. *Reproduction of a beige screen-printing ink.*

Initially, the application of the colour matching theory yielded composition B1. The colour of this ink deviated excessively from the targeted colour ($\Delta E^* = 3.2$). On using this information to adjust the calculation, inks B2 and B3 were obtained, both of which exhibited a difference in colour compared to the reference ink of 0.5 units, which was considered to lie within the acceptance limit, thus ending the colour matching operation.

5.1.2. REPRODUCTION OF A BROWN SCREEN PRINT

Just as in the foregoing section, an industrial ink obtained from a single brown pigment was reproduced.

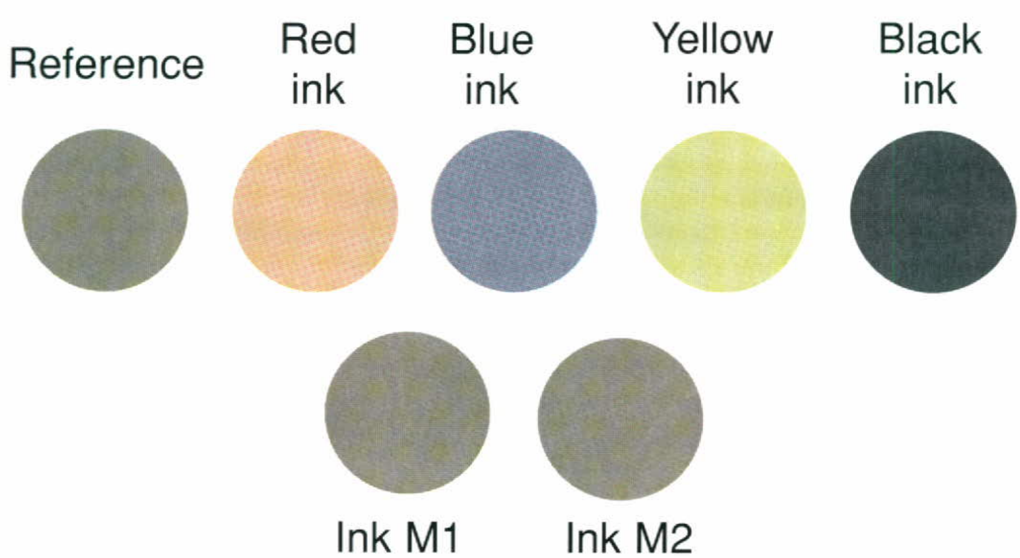

Figure 6. *Reproduction of a brown screen-printing ink.*

In this case, the pigments employed for reproduction were a red, a blue, a yellow and a black pigment. These were used to prepare inks with a high pigment content. Subsequent mixing of these inks yielded the various tested compositions.

Table 2 details the brown reference ink composition, as well as the compositions of the screen-printing inks used in preparing the tested blends.

	Composition						Colour			
Ink	Frit	Pigment					L*	a*	b*	ΔE*
		Brown	Red	Blue	Yellow	Black				
Brown	91.9	8.1					58.7	6.5	9.4	-
Blue	80.0			20.0			54.5	-1.7	-19.1	-
Yellow	80.0				20.0		87.8	-9.7	29.2	-
Black	80.0					20.0	36.8	1.6	-1.7	-
Red	70.0		30.0				67.8	15.3	18.6	-
M1	74.3		17.1		4.6	4.0	59.1	5.7	9.4	0.9
M2	73.0		21.0		2.0	4.0	58.6	6.8	9.2	0.4

***Table 2.** Composition and chromatic coordinates of the inks used in reproducing a brown ink.*

Applying the colour matching theory yielded inks M1 and M2 (Table 2). It can be observed that ink M1 exhibited a colour close to the targeted one, although the result was not considered valid as ΔE* was greater than 0.5. Computation of a new composition, taking into account the foregoing result, produced ink M2. This satisfactorily reproduced the reference colour, in spite of the characteristics of the pigments used being quite different from those of the reference pigment.

The results indicate that the colour matching method allows predicting the composition of a screen-printing ink formulated from various inks of known colour. However, it was shown experimentally that colour reproduction based on these calculations was not wholly accurate, and required making some adjustments. Nevertheless, the number of adjustments was much smaller than usually required.

For this reason, and as will be set out below on discussing the results, in the reference ink reproduction process a series of formulas are obtained that progressively approach the sought-after colour. This adjustment process is considered to have ended when successive adjustments allow no further improvement of results, or when a sufficiently low value of ΔE* (≤ 0.5) is obtained.

5.2. REDUCTION OF THE NUMBER OF PIGMENTS USED

As set out in Section 4, most of the inks used can be obtained by combining pigments form a group of 17 pigments. This entailed an important drop in the number of pigments, compared to the number used previously.

As it is possible to obtain different colours by combining pigments, it was considered convenient to select the minimum number of pigments required to yield the current colour region (Fig. 3). The selection could furthermore be performed so as to also obtain the most economical set of pigments.

Bringing down the number of pigments also provides further advantages by simplifying ink formulation and materials management.

The colour matching methodology described above was used to lower the number of pigments, and it was determined which pigment blends could reproduce other pigments at a lower cost than the initial one. If this constraint were not applied, the reduction in the number of pigments would have been greater, although average pigment price would have been higher.

The calculations were performed by assigning to each pigment a relative cost, determined as the relation between its price and the price of the most expensive pigment. The most expensive pigment thus had a relative cost of one, while the cost of the other pigments was less than unity.

Pigment	Reference	Relative cost
Yellow	PAM1	0.180
Blue	PAZ1	1.000
	PAZ2	0.226
Beige	PBE1	0.188
	PBE2	*0.226*
	PBE3	0.198
	PBE4	0.200
Grey	PGR1	0.2289
	PGR2	*0.499*
Brown	PMA2	0.214
	PMA1	0.259
Black	PNE1	0.609
Red	*PRO1*	*0.305*
	PRO2	0.453
	PRO3	0.233
Green	PVE1	0.321
	PVE2	0.662

***Table 3.** Relative pigment cost.*

Fig. 7 depicts the colorimetric region in which the 17 pigments involved in the study were located. In principle, using the pigments situated at the bounds of this domain allows obtaining all the colours corresponding to the pigments located in the inner area. However, these latter pigments are usually cheaper, so that it is convenient to apply the economic optimisation proposed above.

Taking into account relative pigment costs, it was found that some could profitably be replaced. Thus, pigment PRO1, with a relative cost of 0.305, could be replaced by mixing pigments PRO2, PBE3 and PRO3 at a relative cost of approximately 0.25.

Pigment PBE2, costing 0.226, could be replaced by mixing pigments PAM1, PAZ2, PGR1 and PRO3 at a slightly lower cost (about 0.21).

Pigment PGR2, costing 0.499, could be replaced by mixing pigments PNE1, PRO2, PAZ2 and PGR1 at a relative cost of about 0.26.

Thus, the number of elementary pigments could be cut back to 14.

It can be observed that the reduction in the number of pigments has not been excessively great, indicating that the current ink formulation system has, after a great number of trials in industrial practice, been able to identify a set of pigments quite close to the optimum group found. The fact however that the proposed colour matching method has allowed defining an optimum system so rapidly underscores the method's efficiency.

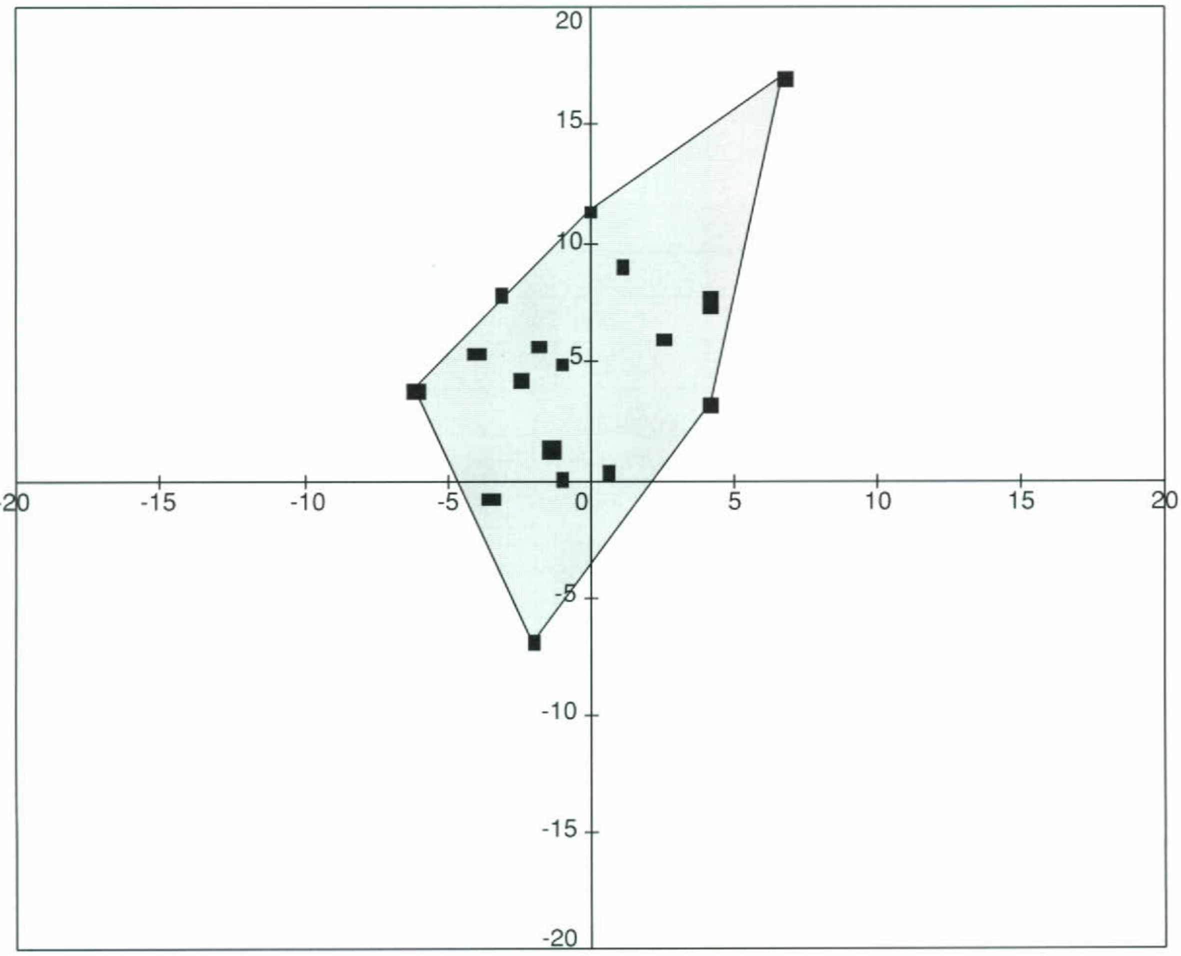

Figure 2. *Colour space region in which the tested inks were located.*

5.3. INK PREPARATION METHOD

The results obtained in the foregoing sections, indicated the validity of the colour matching techniques for the screen-printing inks used in ceramic tile manufacturing. This has enabled modifying the preparation method of these inks, both in production and in the design laboratory.

The industrial ink preparation procedure would therefore consist of the following stages (Fig. 8):

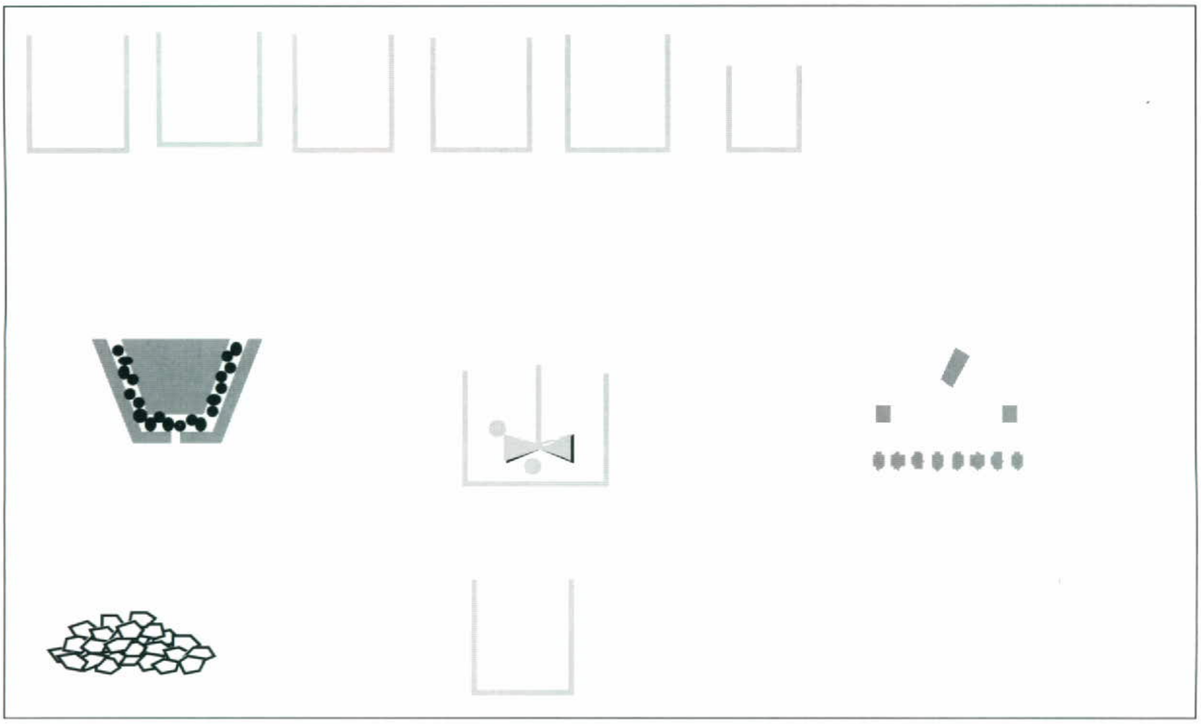

Figure 8. Schematic of the proposed preparation methodology.

1. Preparation of concentrated pigment and base suspensions. These just contain a vehicle and a pigment, or a vehicle and a frit. Both types of suspension are made up according to the steps set out in the introduction (proportioning - mixing - dispersing). After making up the suspensions, the colour obtained needs to be accurately determined, since this information will subsequently be used in preparing the inks. The prepared suspensions are stored in tanks till used.

2. Calculation of the ink composition, proportioning and mixing of the suspensions that form the composition. In this case, the ink constituents are proportioned in a liquid state, so that the process can be readily automated, while keeping high accuracy. Blending is almost instantaneous.

3. Colour adjustment. If the ink prepared on the basis of the calculations does not exactly yield the targeted colour, the formula needs slight adjustment. The technique used in this study allows obtaining the desired colour by one or two adjustments, which is considered acceptable. Obtaining a targeted colour in the first formulation would mean having the whole decorating and firing process running under exactly the same conditions as those that were in place when the

original pigment suspensions were characterised, which would be highly unlikely.

With this approach, pigment suspension preparation can be performed continuously, without the typical conditioning factors of the production process. This allows planning the preparation of each pigment suspension in larger batches than the present ones, with more efficient dispersion equipment operation. Moreover, such planning brings down the number of dispersion equipment cleaning operations. These take place whenever the ink is changed, which means that there is less materials waste, and less waste from the cleaning operation itself.

On putting a model into production, it is only necessary to mix the required proportions of the respective pigment and base suspensions, without again having to refine the ink after each adjustment. Furthermore, using the calculation technique set out above for matching colour reduces the number of adjustments.

The colour matching method also makes it possible to wholly reclaim screen-printing ink rests, since knowing their colorimetric characteristics allows them to be easily reused in formulating new inks. This also entails savings in the materials used in the inks, while the production process assimilates a waste product whose disposal would otherwise have involved certain costs.

The colour matching method could be also used in the design steps: when the colour to be reproduced is selected, its colorimetric attributes (L^*, a^*, b^*) can be determined, and the elementary pigments mixture that will yield this colour can be calculated by this colour matching method.

In this sense, it would be particularly interesting for the company to prepare a colour palette that would basically involve the colours used in most of the designs. This would drastically cut down the work required for developing colours and allow the company departments involved to focus on design.

6. CONCLUSIONS

The present study allowed drawing the following conclusions:

The colorimetric region occupied by the most commonly used inks in tile manufacture was determined. The region involved was shown to be quite small.

A calculation method was put forward for producing screen-printing ink colours on the basis of the Kubelka-Munk theory. The method takes into account pigment cost in order to obtain the economically optimum blend.

A detailed analysis of the ink formulas used permitted directly reducing the number of pigments by 40%, which greatly simplifies materials management and ink formulation.

Application of the colour-matching technique set out in the study allowed reducing the number of pigments used even further, as well as lowering average pigment cost.

A new ink preparation system was proposed, which besides other advantages yields more efficient use of ink preparation equipment, reduction in arising waste, and considerable simplification and acceleration of ink make-up in production.

The system also allows reusing the typical ink residues in new ink formulations, lowering materials consumption and waste.

The colour matching technique involved is also considered to be a very powerful tool for design development laboratories, as it allows fast and simple reproduction of any colour.