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Colour in ceramic glazes: Efficiency of the Kubelka–Munk model in glazes with a black pigment and opacifier

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Abstract

In this study the efficiency of the Kubelka–Munk model (already known and consolidated in other industrial sectors) was evaluated in the prediction of the colour of an opaque ceramic glaze obtained by a mixture of black pigment (spinel Ni–Fe–Cr) and zircon opacifier ($ZrSiO_4$). Glazes with different percentages of black pigment and opacifier were prepared to determine the absorption and scattering optical constants from the reflectance curves measured with a spectrophotometer. After the physical and chemical characterization of the glaze components (frit, pigment and opacifier), suggestions for the adaptation of the Kubelka–Munk model were made to facilitate the experimental procedure of analysis. The result obtained with the adapted Kubelka–Munk model was in good agreement with the experimental reflectance curves. The reproduction of the desired colour was possible with a reduced number of experiments and the model made it possible to correlate the colour with the added pigments concentration facilitating the formulation step.

Keywords: Colour; Spectroscopy; Grain size; Optical properties; Traditional ceramics

1. Introduction

In ceramic glazes the colour is obtained by the dispersion of pigments and opacifiers. The formulation, as well as the adjustment of glaze colour, in the ceramic tile industry is still empirical, making its control difficult. The colour control is usually performed using the CIELab system, through the measure of L^*, a^*, b^* parameters, even though this system has some limitations.[1] Infact there is not a systematic relation between the L^*, a^*, b^* values and the concentration of added pigments. The Kubelka–Munk[2] model, already known and applied in the textile and paint sectors and recently utilized in the ceramic sector,[3,4] is the way to relate the colour (reflectance) with the concentration of the added pigments. The Kubelka–Munk model results in the equation:

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

where R is the fractional reflectance, K is the absorption coefficient, and S is the scattering coefficient at each wavelength of light in the visible region (400–700 nm). This simple relationship can be applied to thick opaque plastics, to paints with complete coverage, and to opaque ceramics.[5] Duncan[6] demonstrated the additivity of the individual contributions of absorption and scattering in a mixture, M, at each wavelength:

$$f(R) = \left(\frac{K}{S}\right)_M = \frac{c_1K_1 + c_2K_2 + c_3K_3 + \cdots}{c_1S_1 + c_2S_2 + c_3S_3 + \cdots} \tag{2}$$

where K/S is the light absorption caused by a mixture of pigments; c_i are the concentrations of the pigments added to the formulation; K_i and S_i are, respectively, the absorption and scattering coefficients and R is the reflectance measured by a spectrophotometer. When the K_i and S_i values are determinated

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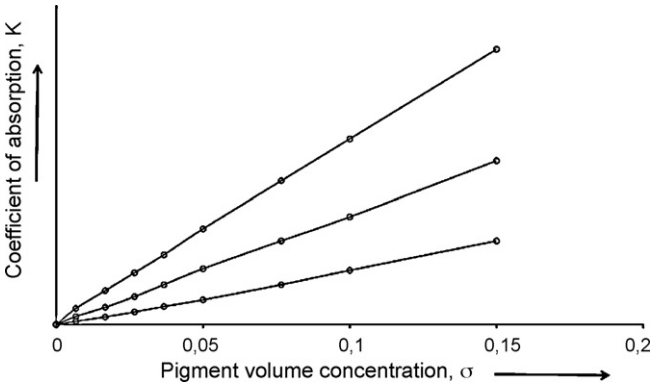

Fig. 1. Absorption coefficient K for diffuse illumination as a function of the pigment volume concentration for three red iron oxide pigments (from Ref. [8]).

at each wavelength in the visible region for the i pigment, the relation K/S of the mixture can be predicted, and consequently the reflectance of the mixture.[3]

The simple equation (1) states that if the absorption, K, is increased and the scattering, S, is kept constant, the reflectance is decreased. For instance the addition of a strongly absorbing pigment, such as black, to a system decreases its reflectance; while if S is increased keeping K constant, the reflectance is increased. Thus adding to a system a strongly scattering pigment, such as white, the reflectance increases; if both the absorption and scattering are changed by the same quantity, this will not affect either the resulting reflectance or the colour. Remembering that the nature of the colour is described by its spectrophotometric curve and that at each wavelength the Kubelka–Munk model describes how the reflectance is determined, one can visualize how the curve may be modified in a desired way.[5,7]

The behaviour of the optical constants of the Kubelka–Munk model with the amount of pigment added to a mixture confirms that the absorption coefficient K follows a Beer's law[8] even at high pigment volume concentrations being therefore proportional to the volume fractions, σ (Fig. 1). However, the determination of the relationship between the scattering coefficient, S, and the pigment concentration implies some problems. When the concentration increases the distance between the pigment particles decreases causing an interaction and hindrance between the light scattered by individual particles an effect which is translated in the fall of their scattering power. Therefore only at low pigment concentration is the scattering coefficient S linearly related to concentration (the Beer's law region) while at higher concentration it remains below the linear value (Fig. 2).

For the above reasons the analysis of the physical interactions between pigments, opacifier and glazes is fundamental to understand the optical behaviour of ceramic glazes. Really the hue variations can be caused by process variables,[9] e.g., pigment and opacifier preparation conditions that affect the pigment and opacifier physical and chemical properties.[10,11] In particular the pigment and opacifier grain size distribution and their refraction indexes are fundamental to determine the optical properties of the glazes directly changing the colour of the product.[10] The grain size distribution has a very important role: pigments/opacifier with large particle size have, as a consequence, a reduced coating power, while smaller particle sizes tend to diminish the intensity of the colour and/or to produce different shades tending to easily dissolve into the glaze. Furthermore there is an increase of the white light scattering resulting in a decrease of colour saturation.[11,12] Moreover, the refractive index of the crystal structure is important because both the colouring power and the opacification depend on it. The most currently used opacifier is zircon ($ZrSiO_4$). It has an high refraction index (1.96) and is considerably more inexpensive than titanium dioxide, largely used also as opacifier.[11]

In this work the efficiency of the Kubelka–Munk model was evaluated in the prediction of the colour of an opaque ceramic glaze obtained by a mixture of black pigment and zircon opacifier ($ZrSiO_4$). In particular the model was adapted considering the peculiarity of the studied system.

2. Corrections to the Kubelka–Munk method

In this work a simplification of the Kubelka–Munk method was used because the opaque glaze chosen contains a frit that during firing devitrifies to form zircon crystals. In this case the glaze can be considered as a component of the mixture in the Kubelka–Munk model that becomes[13]:

$$\left(\frac{K}{S}\right)_M = \frac{c_g K_g + c_p K_p + c_o K_o}{c_g S_g + c_p S_p + c_o S_o} = \frac{(1-R)^2}{2R} \tag{3}$$

where the subscripts g, p and o are referred to glaze, pigment and opacifier, respectively. Considering that the scattering of zircon crystals formed in the glaze and added as opacifier is the same, as they have the same refraction index ($S_g = S_o = 1$), the Kubelka–Munk model for these mixtures can be simplified[13]:

$$\left(\frac{K}{S}\right)_M = \frac{c_g K_g + c_p K_p + c_o K_o}{c_g + c_o + c_p S_p} \tag{4}$$

To determine the coefficients of Eq. (3) it is necessary to measure the reflectance curves and to calculate the K/S ratio of four glazed samples: one sample prepared only with the glaze (to determine K_g), one sample with a fixed percentage of opacifier (to determine K_o), one sample with a fixed percentage of pigment

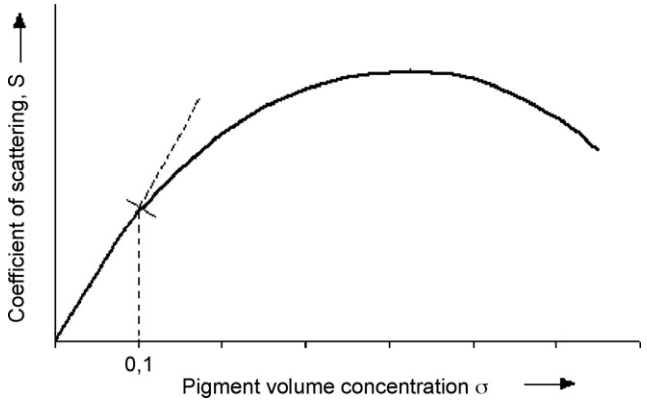

Fig. 2. Scattering coefficients as a function of the pigment volume concentration (from Ref. [8]).

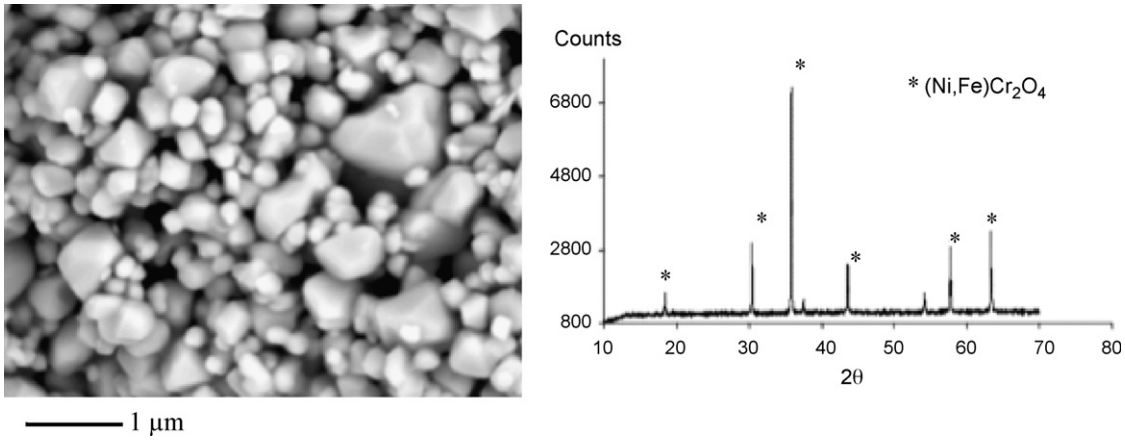

Fig. 3. SEM micrograph and X-ray diffraction pattern of the used pigment.

and one sample with a mixture of pigment and opacifier. The total load added in the glaze must be the same in all samples.[13]

In particular, the measure of the reflectance curve of the sample formed by glaze and opacifier makes it possible to calculate $(K/S)_{go}$, and thus to obtain K_o by the expression:

$$K_o = \frac{(K/S)_{go} - c_g K_g}{c_o} \tag{5}$$

where c_g and c_o are the concentrations of the glaze and opacifier, respectively.[13]

The measure of the reflectance curve of the sample formed by glaze and pigment makes it possible to calculate the $(K/S)_{gp}$ and to obtain K_p by the expression[13]:

$$K_p = \frac{c_g}{c_p}\left(\left(\frac{K}{S}\right)_{gp} - K_g\right) + \left(\frac{K}{S}\right)_{gp} S_p \tag{6}$$

Finally, the measure of the reflectance curve of the sample formed by a mixture of glaze, opacifier and pigment yields S_p[13]:

$$S_p = \frac{x_g/x_p((K/S)_{gpo} - K_g) + x_o/x_p((K/S)_{gpo} - K_o) + c_g/c_p(K_g - (K/S)_{gp})}{(K/S)_{gp} - (K/S)_{gpo}} \tag{7}$$

where the x_g, x_o and x_p are the concentrations of the glaze, opacifier and pigment added in the sample.[13]

Hence, with these four samples it is possible to determine the coefficients of Eq. (3) and to predict the colour of the glazes as a function of the concentration of black pigment and opacifier added in the glazes.

Table 1
Chemical composition of the opaque frit used in the study.

Oxide	Wt%
SiO_2	56.00
ZrO_2	7.40
ZnO	9.60
Al_2O_3	5.07
R_2O ($K_2O + Na_2O$)	3.40
RO (CaO + MgO)	12.80
B_2O_3	5.65
Fe_2O_3	0.08

3. Experimental procedure

The coloured glazes were prepared using industrial grade raw materials as kindly received by Ferro Brazil. The pigment used in this work was characterized by X-ray diffraction analysis (XRD, PW 3710, Philips Research Laboratories) and by scanning electron microscopy (SEM, XL 30 Philips) equipped with an X-ray

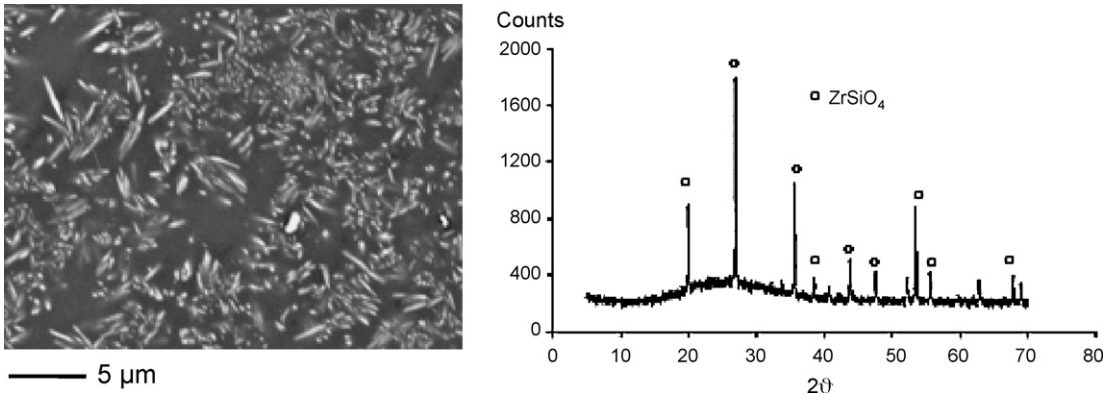

Fig. 4. SEM micrograph and X-ray diffraction pattern of the glaze after firing.

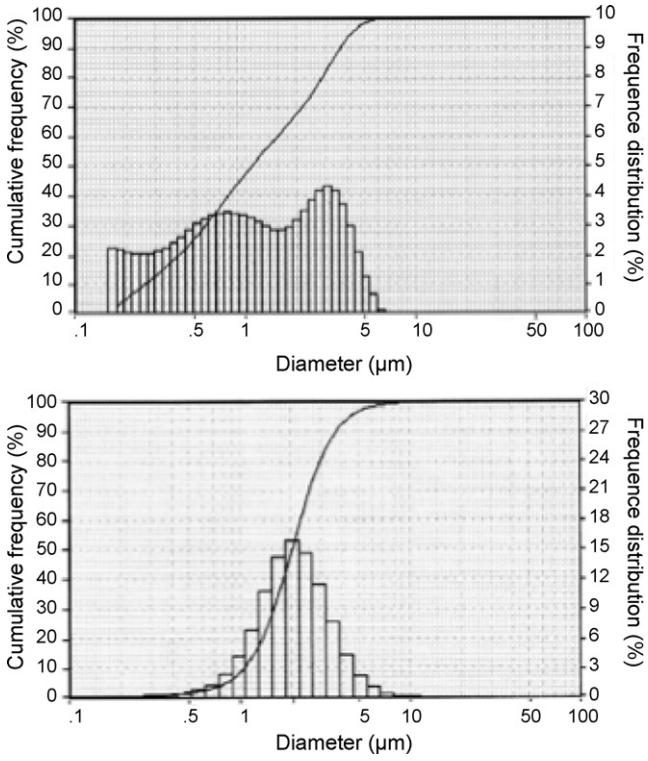

Fig. 5. Granulometric distribution of (a) opacifier and (b) black pigment added in the glaze.

energy dispersion spectroscopy (EDS, INCA). Fig. 3 shows that the black pigment is a Ni–Fe–Cr spinel, (Ni, Fe)Cr_2O_4, with an homogeneous grain size distribution as confirmed by scanning electron microscopy and the X-ray diffraction analysis (Fig. 3).

Fig. 6. Examples of prepared black glazes (5, 3, 2.5 and 1% of black pigment).

Table 2
Concentration of pigment and opacifier in the four glazes prepared to determine the Kubelka–Munk constants and respective colorimetric data.

	(Ni, Fe)Cr_2O_4 Pigment (%)	$ZrSiO_4$ (%)	L^*	a^*	b^*
Black glazes	5.0	–	34.19	0.32	−3.92
	2.5	2.5	45.22	0.04	−4.45
Glaze + opacifier	–	5.0	96.18	−0.68	2.16
Glaze	–	–	96.01	−0.87	2.55

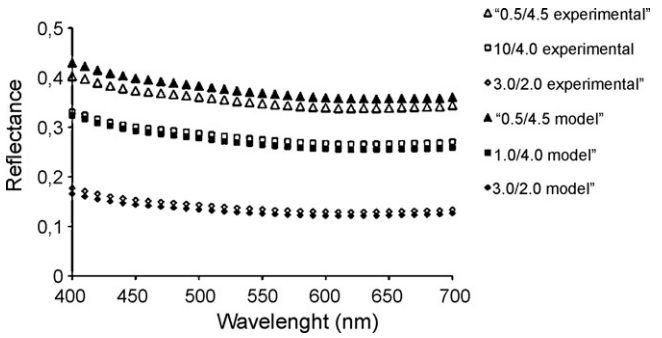

Fig. 8. Reflectance curves obtained experimentally in comparison with that determined by the Kubelka–Munk model for same glazes prepared.

The frit used in this work was an opaque frit (chemical composition in Table 1) that during firing devitrifies to form zircon, $ZrSiO_4$, crystals as verified by scanning electron microscopy and the X-ray diffraction (Fig. 4). Regarding the grain size distribution, measured with a laser granulometer (Fritsh, model Analysette 22), the black pigment presents a monomodal curve with medium particle size of 2.03 μm, whereas the opacifier presents a bimodal distribution with medium particle size of 1.0 μm (Fig. 5).

The glazes were prepared in a laboratory ball milling with: 92 wt% opaque frit, 8 wt% and different percentages of black pigment and industrial zircon, $ZrSiO_4$, opacifier. To determine the Kubelka–Munk constants four different glazes were prepared as described in Section 2 (Table 2). The wet milling was made with 50% of water in a ball mill for 20 min. After drying, cylindrical samples (25-mm diameter and 6-mm thick-

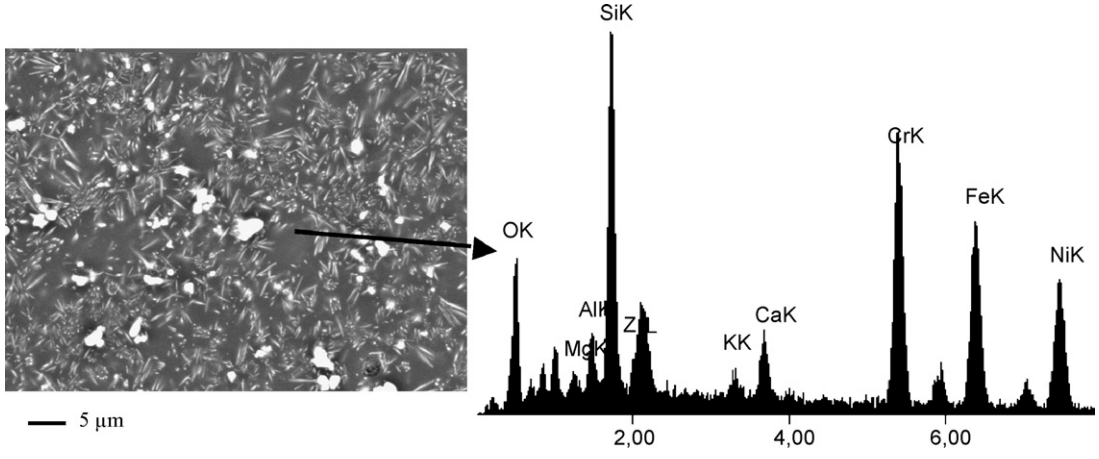

Fig. 7. SEM micrograph of the glaze with 5% of black pigment and EDS spectra of the pigment particles.

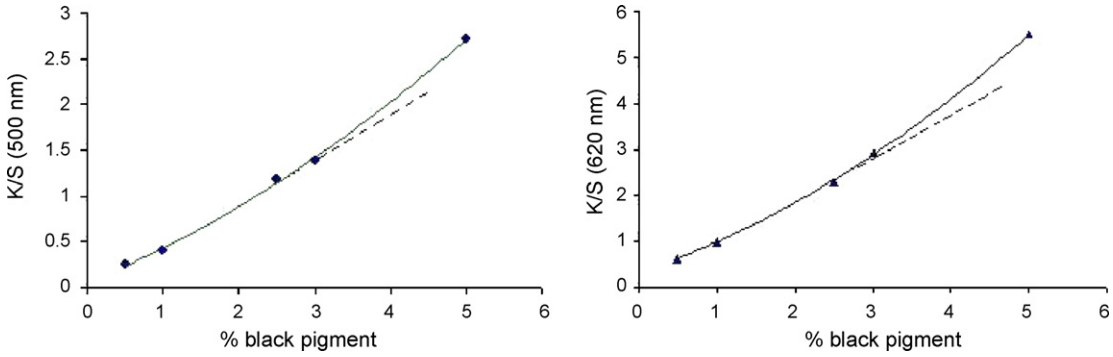

Fig. 9. Kubelka–Munk absorption as a function of the black pigment (spinel Ni–Fe–Cr) concentration in the glaze.

Table 3
Concentration of pigment and opacifier in the glazes prepared to evaluate the efficiency of the Kubelka–Munk model and respective colorimetric data.

	(Ni, Fe)Cr_2O_4 Pigment (%)	$ZrSiO_4$ (%)	L^*	a^*	b^*
Black glazes	3.0	2.0	43.63	0.01	−4.46
	1.0	4.0	59.57	−0.23	−3.81
	0.5	4.5	65.71	−0.23	−3.37

ness) of glazes were prepared by pressing the powder (6 wt% of water) with a laboratory press. The samples were fired in a semi-industrial kiln at maximum temperature of 1175 °C ± 10 °C with a cycle of 35 min. L^*, a^*, b^* parameters and the reflectance curves of the fired samples were measured by a Datacolour-Spectraflash 600 spectrophotometer with optical geometry d/8, illuminant D65 and observer 10°. The microstructure of the glazes was determined with a Philips scanning electron microscope (SEM, Philips model XL 40 equipped with a EDS) in order to verify the dispersion of the pigment into the glaze.

Finally other three glazes (Table 3) were prepared with the same procedure to evaluate the efficiency of the Kubelka–Munk model to predict their reflectance curves.

4. Results

Fig. 6 shows some samples produced after firing; Fig. 7 shows the microstructure of the glaze with 5 wt% of Ni–Fe–Cr spinel pigment and the EDS analysis that identifies the dispersed pigment particles. The pigment presents do not modify the frits thermal behaviour since the acicular crystals are the zircon crystals formed during firing by frit devetrification.

Using Eq. (1) from the reflectance curves of the prepared glazes, the K/S values were calculated at each wavelength of visible region and the obtained curves were utilized to determine the Kubelka–Munk constants (at each wavelength of visible region) using Eqs. (5)–(7) as described in Section 2. The obtained values, inserted in Eq. (4), allowed the glaze colour prediction for every pigment and opacifier concentrations. The reflectance curves predicted by Kubelka–Munk model for the glazes reported in Table 3 are showed in Fig. 8 in comparison with the experimental data. An excellent agreement between the experimental and the calculated curves was observed with deviations lower than 2.0%.

Finally, the obtained results confirm that there is not a systematic relation between the L^*, a^*, b^* values and the concentration of added pigments (Tables 2 and 3). As expected the L^* parameter (lightness) decreases as the pigment concentration is increased due to the major quantity of pigment particles that absorb light. a^* and b^* parameters, instead, have changes difficult to interpret. In Fig. 9 the values of Kubelka–Munk absorption at 620 and 500 nm, chosen as representative, are reported. The linear behaviour indicates that with the Kubelka–Munk model it is possible to systematically relate the colour to the quantity of added pigment. In particular the figure illustrates that the K/S value increased as the quantity of the pigment is increased with a small non-linear tendency starting from 3.0% concentration of black pigment. Since the added black pigment has a high light absorption power and small particle size (as shown in Fig. 5), the inconvenience of the interaction between S and pigment concentration is confirmed. For pigment amount higher than 3% the scattering coefficient (S) is lower than the linear value because the distance between the pigment particles decreases. This phenomenon causes an interaction between the light scattered by individual particles that determines an exponential increase of the K/S relation.

5. Conclusions

Even if the L^*, a^*, b^* parameters are used in the control and formulation of colour of ceramic glazes, it is difficulty to evaluate their behaviour with the concentration of added pigments. With the proposed Kubelka–Munk model it is possible to relate the colour with the concentration of the black pigment and opacifier added and to make predictions of the colour produced with a good accuracy.

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