ANALYSIS OF TONALITY VARIATION IN CERAMIC TILES USING SPECTROPHOTOMETRY

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ABSTRACT

Nowadays shades are a major problem in the Brazilian ceramic industry. Quality control is made using visual inspection and comparison with colour standards. Visual inspection depends on the observer's ability to determine if a product is inside or outside the acceptable limits of colour deviation, defined by the colour standards.

Visual inspection for standard comparison is useful only for deviation identification, but not for quantification. Thus, it is necessary to use optical devices like colorimeters or spectrophotometers, as they eliminate the sources of variation; they thus standardize evaluation conditions like illumination, environment and colour identification.

This work deals with tonality deviation in ceramic tiles processed by the single-firing technique. Three inorganic pigments were used: a red one, based on Zr-Fe oxides; yellow, based on Zr-Pr oxides; and blue, based on Zr-V oxides. The three pigments were added to a white glaze matrix in fractions of 1%, 3% and 5%, all in weight. The obtained enamels were then fired at 1130°C for 4 min (at this maximum temperature). After firing, the glaze layers of the samples were analyzed using optical microscopy; colour development and tonality variations were determined using spectrophotometry.

Key words: *tonality; ceramic tiles; spectrophotometry; enamels.*

1. INTRODUCTION

Nowadays tonality repeatability has not yet been achieved in the production of ceramic tiles, resulting in a quite large amount of tonalities per product reference, and products with inferior classification [1, 2, 3]. The problem of tonality variation does not have a simple solution, because many factors influence this characteristic. Research related to this problem is practically non-existent in Brazil. Thus, it is necessary to search for methods that identify the causes of the variation of tonality and to characterize coloured ceramic tiles, in order to minimize the problem and increase production efficiency [4, 5].

2. COLOUR DEVELOPMENT IN CERAMIC MATERIALS

Glaze colour is a result of absorption of part of the incident light from visible radiation and the reflection of only certain wavelengths, which results in the different perceived colours [6]. Red is perceived as red because the glaze absorbs all the wavelengths, except the ones corresponding to the red colour; a black object absorbs all the wavelengths and a white object reflects all the wavelengths of the visible spectrum. To colour a ceramic glaze it is necessary to combine in the glaze structure individual calcined pigment particles, of microscopic size [7].

For the ceramic industry more important than identifying a specific colour is the ability to measure the differences between this and other colours. Colour control is especially significant in the evaluation of glazes and decorative colour quality. Though the final consumer always decides by visual inspection, pigment suppliers and users cannot avoid the use of colour measuring techniques. On the other hand, there are tonality differences only perceivable with instruments; for example, small variations in glaze preparation related to the milling process (amount of crushing material, kind of material to be milled, kind of water, milling speed, etc.) can influence in a non-perceivable way for the human eye, the tonality of the milled glaze. Tonality control and adjustment of coloured glazes are a main problem in ceramic tile industry [1, 2].

The property that characterizes colorants and pigments is the way they preferentially absorb (subtract) some fractions of incident light of a specific wavelength and, considering that the incident light is essentially white, the coloured objects show the complementary colour related to the absorbed light. The preferential absorption of the light gives the reflectance spectrums of coloured objects, i.e., its characteristic appearance (as "fingerprints"). Colour is a combination of three parameters: tonality, luminosity and chromaticity. Colour is a question of perception and subjective interpretation [7, 8].

To identify the same colour, different people can base their evaluations on different references and express them with different words. This is related to the existence of many varied expressions to identify a particular colour, and colour identification becomes difficult and vague. To express a colour is very complicated and inexact. Thus, it was necessary to have a method in which the colours could be accurately expressed and the explanation of these colours could be simpler and correct. Colour determination using spectrophotometers is more accurate and trustworthy than colour expression by human perception and words.

3. COLORIMETRY

Colorimetry is the Science of light measurement in its aspects of colour, luminosity and chromaticity; it studies all colour vision relative phenomena, to which not only Physics and Psychology contribute, but also Chemistry, Biology, Anatomy, Neurology, etc. Colorimetry sets out to specify light colours, or light emitted from objects in a scientific, practical and relatively simple way. Colorimetry aims to determine the concentration of a specific substance by the measurement of its relative light absorption, taking as reference the absorption of the substance in a known concentration. In visible region colorimetry, a natural or artificial source of white light is used in general as a light source. The measurements are carried out in a simple instrument, called a colorimeter, or colour comparator. When the human eye is replaced by a photoelectric cell, which to a large extent eliminates the errors due to the personal characteristics of each observer, the instrument is a photoelectric colorimeter [9].

The relative intensity of the light that a material transmits, reflects and absorbs is a function of the wavelength of the incident light; thus, the colour characterization of a specific material is possible from the plot of the respective transmittance, reflectance or absorbance curves in function of the visible light wavelengths. To obtain such curves, spectrophotometers or spectrocolorimeters can be used. The light emitted from a source reaches a monochromator (generally a prism) which allows selecting in a continuous form, by rotation, the radiations of the luminous spectral interval of interest. The light that crosses the sample is collected in a phototube that transforms it into an electric current proportional to the intensity of the transmitted light, whose relation with the wavelength is traced in a graph (or spectrum) [7], [8], [9].

4. MATERIALS AND METHODS

Initially a glaze matrix composed of a zirconia (zirconium oxide) based white frit and kaolin was formulated in the proportion of 90 wt% frit and 10 wt% kaolin; this standard glaze was then milled in laboratory ball mill (eccentric type) for 50 minutes with 40 wt% water addition.

To this standard glaze three ceramic pigments were added in fractions of 1 wt%, 3 wt% and 5 wt%; the pigments are silicates of zirconium-praseodymium (yellow colour), zirconium-vanadium (blue) and zirconium-iron (red) systems. Homogenization was made by means of a laboratory agitator.

The pigmented glazes were then applied with an air pistol to the previously engobed and pre-fired ceramic tiles (10cm x 10cm); the glazed tiles were dried (110°C) and fired in a laboratory kiln with a one hour cycle at a maximum temperature of 1130°C, and four minutes hold at this temperature.

Finally, the fired glazed tiles were analyzed in a spectrophotometer with a wavelength resolution between 400nm and 700nm with 10nm increments, 45/0 geometry, without ultraviolet filter. The spectral curves correspond to an average of five readings of each sample; five samples for each condition (combination of pigment type and amount) were analyzed.

5. RESULTS AND DISCUSSION

Zirconia glaze samples with the addition of red (Zr-Fe system), yellow (Zr-Pr system) and blue (Zr-V system) pigments are shown in figures 1, 2 and 3, respectively. As expected, the colour intensity (chromaticity) increases with pigment addition from 1 wt% to 5 wt%.

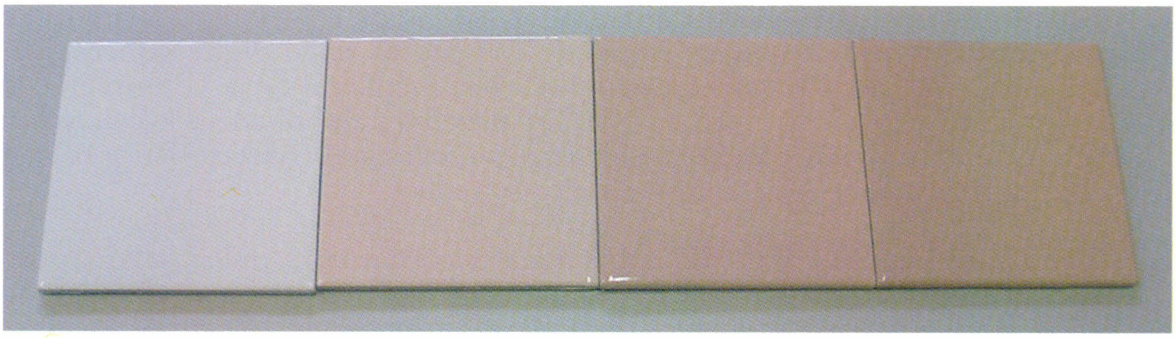

Figure 1. Samples of glazed ceramic tiles with the red pigment.

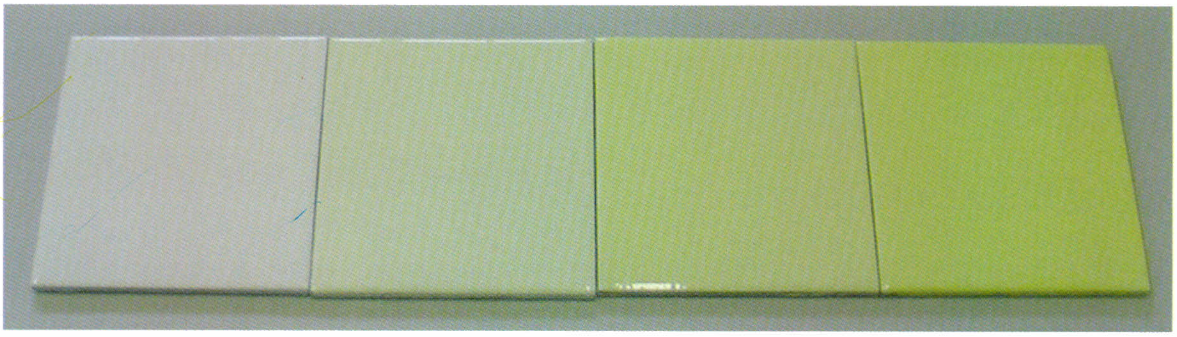

Figure 2. Samples of glazed ceramic tiles with the yellow pigment.

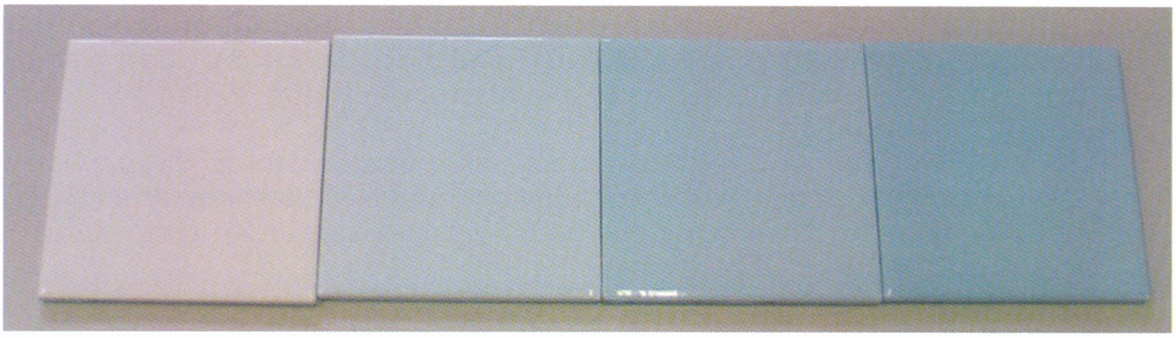

Figure 3. Samples of glazed ceramic tiles with the blue pigment.

The colour spectrum of the white glaze is shown in figure 4 – glaze based on white zirconia frit and kaolin, applied on engobed ceramic tiles.

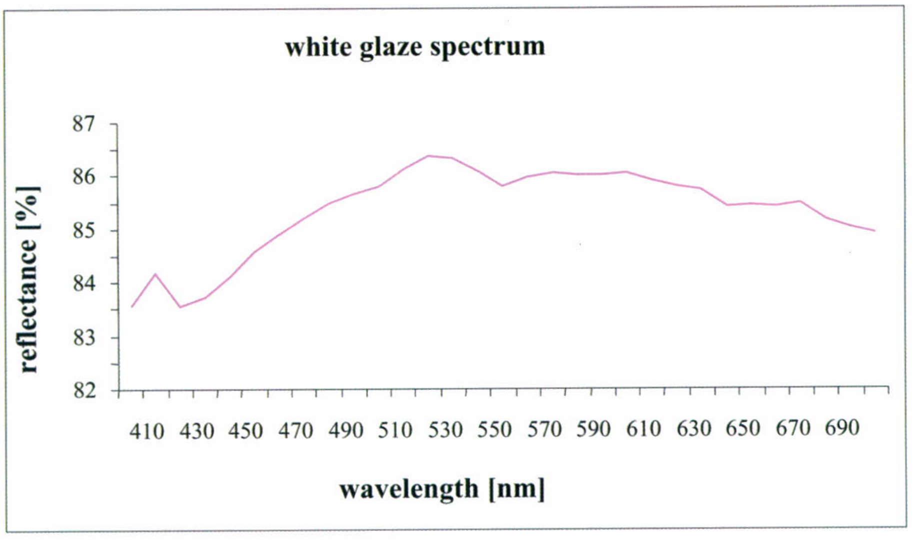

Figure 4. Reflectance spectrum for the white enamel, without pigment addition.

The reflectance variation for the white samples (tiles on the left in figures 1 to 3) is in an interval between 83.5% and 86.6%, corresponding to a smooth grey colour, with a tenuous yellow pigmentation – the reflectance increases slightly beginning at 500nm, remaining thus until 700nm.

Figure 5 corresponds to the reflectance curve spectra for the red pigment, added in fractions of 1 wt%, 3 wt% and 5 wt%. With the pigment addition increment from 1 wt% to 5 wt% a reduction occurs in the reflection in all the wavelengths, both for the Zr-Fe (red) and Zr-V (blue) systems; this corresponds to an increase in the chromaticity of the samples, figures 5, 6 and 7.

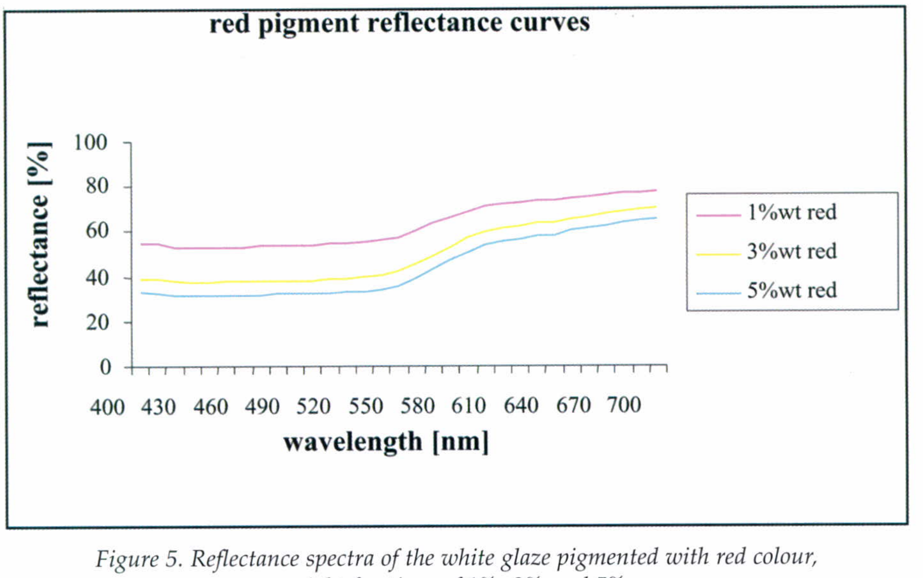

Figure 5. Reflectance spectra of the white glaze pigmented with red colour, weight fractions of 1%, 3% and 5%.

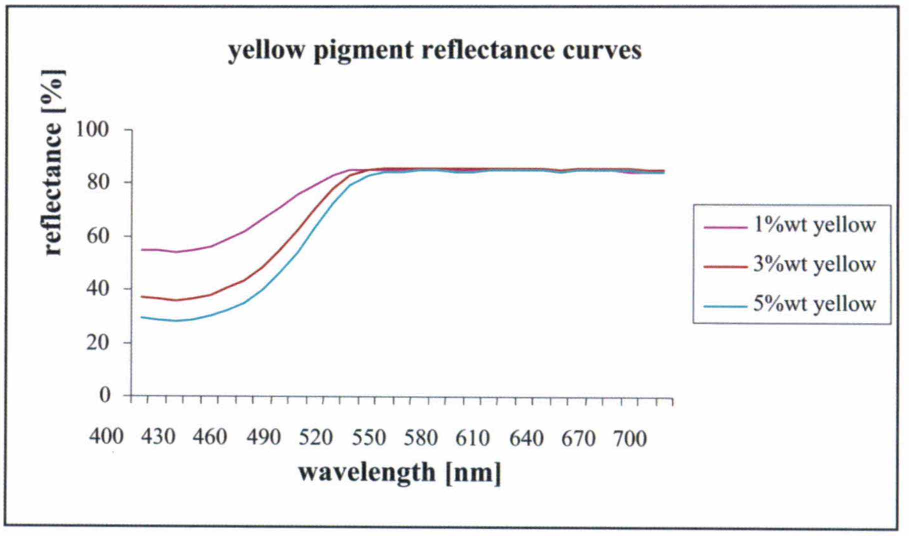

Figure 6. Reflectance spectra of the white glaze pigmented with yellow colour weight fractions of 1%, 3% and 5%.

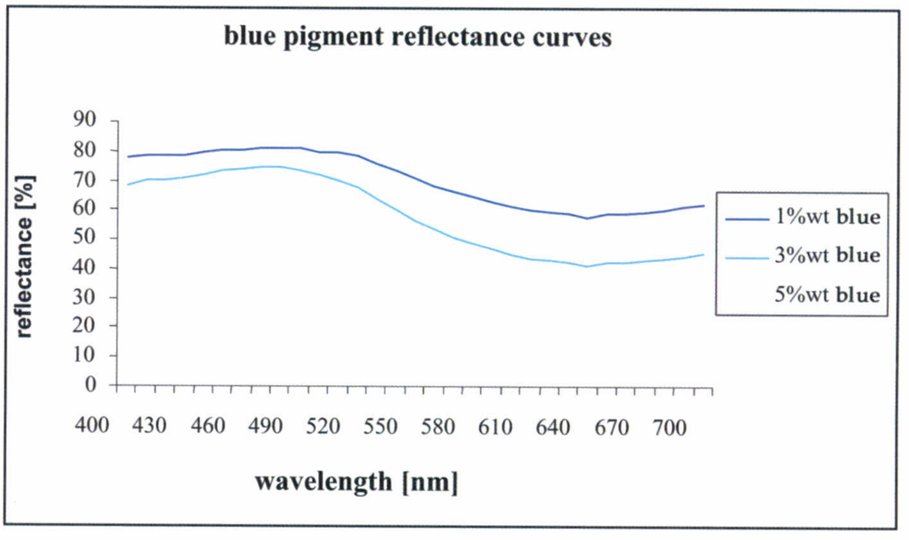

Figure 7. Reflectance spectra of the white glaze pigmented with blue colour weight fractions of 1%, 3% and 5%.

However, for the yellow pigment a reduction in the reflectance with pigment addition occurs only for wavelengths below 550nm.

6. CONCLUSION

The spectrophotometer technique is very adequate for analysis of tonality variation in ceramic tiles. Despite the large wavelength increments of the equipment used, about 10nm, which corresponds only to 32 points in the range between 400nm and 700nm, the spectral curves obtained were well defined, and it was possible to distinguish the reflection behaviour of the analyzed samples.

The sample base, a white glaze, to which the pigments had been added, presented a typical luminosity of a smooth grey. It is probable that this luminosity

(85% reflection average) would be responsible for the sharp reflectance loss of the analyzed samples for the three pigments. Perhaps bigger luminosities (above 90%) would represent a lesser degree of reflectance reduction for the same amount of added pigments.

Finally, for a more complete analysis of the pigment addition effect on the glazes opacified with zirconia, a microstructural analysis would be necessary of the samples to verify the pigment dispersion in the glass matrix.

7. ACKNOWLEDGMENTS

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