INFLUENCE OF FIRING CONDITIONS ON THE ARISING COLOUR DIFFERENCE (TONALITY) IN CERAMIC GLAZES

Partyka Janusz, Gajek Marcin

AGH Cracow University of Science and Technology, Department of Materials Science and Ceramics, Poland

ABSTRACT

Colour differences (tonality) play a very important role in the ceramic industry, especially with regard to product quality and market expectations. Tonality issues relate not only to the final product but also to the semi-finished products (coloured bodies, engobes, glazes, screen printing pastes or inks). Maintaining the production technological regime is a key factor in producing high quality ceramic products. The present work attempts to answer the question how the firing conditions can influence the colour differences that arise in the surface of ceramic tiles. The investigations dealt with one glaze composition, which was prepared in various grain size distributions and was coloured using two pigments, beige and dark brown. The preparation procedure of the coloured glaze was different in the mixing technique, as well as in the mixing time. The glazed samples of floor tiles were fired in three different firing curves, which differed from each other in maximum temperature and dwell time. These differences occur in industry very often.

1. INTRODUCTION

Colour in ceramics results from applying inorganic synthetic pigments or some oxides to bodies, glazes, screen printing pastes or inks. Colour difference, often described as tonality, is one of the most difficult problems in the ceramics industry. That is, how to obtain and maintain the standard quality of colours (*glaze, decoration, bodies*) or how to reduce the colour difference (tonality). The problem with colour differences occurs mainly in restarting the production of a particular batch or in the long-term continuous production of the certain products (*which requires the repeated preparation of glaze and decorative materials*). This paper attempts to define the firing conditions and certain very important parameters that influence the tonality of ceramic products, and to provide a few tips to ensure their stability and repeatability.

2. EXPERIMENTAL PROCEDURE

The main objective of the present paper is to define how the firing conditions can influence the colour difference in coloured glazes, when other parameters are constant. This is compatible with the main concept of research work, in which the variability of only one parameter is assumed, while all others should be constant.

To carry out this work, the following materials and conditions were used:

- three batches of commercial ceramic matt glaze, varying in grain size distribution (Fig. 1). Coarse (gsd-1) with an average grain size of 4,2 μm, intermediate (gsd-2) with an average grain size of 3,0 μm, and fine (gsd-3) with an average grain size of 1,8 μm. Grain size distributions were measured using Micromeritic 5100;

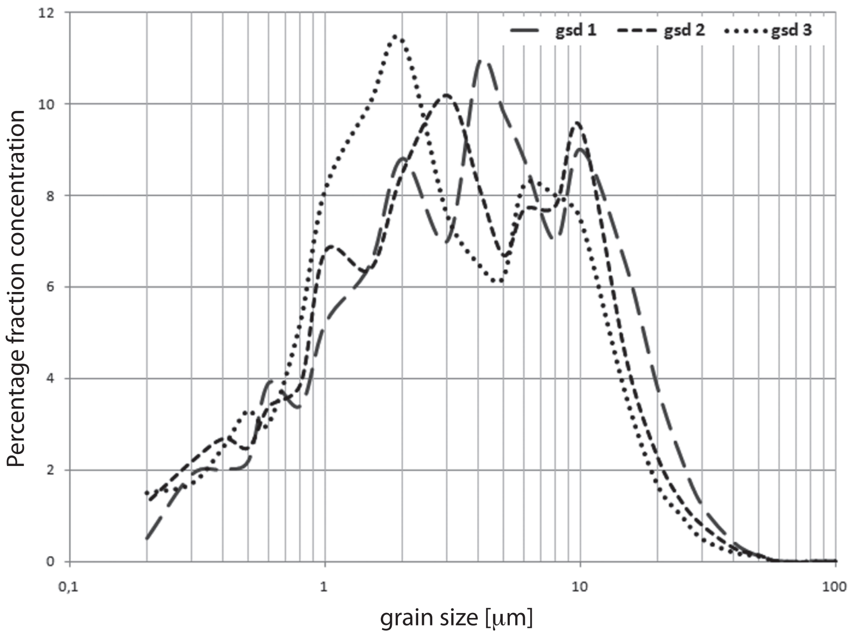

Fig. 1. Grain size distribution of the experimental glazes.

- two ceramic pigments: dark brown and beige, sensitive with regard to creating colour differences, added in quantities of 1, 2 and 3% by weight;
- two types of stirrers for preparation of the coloured glazes: high-energy and low-energy stirrers. By the "high-energy stirrer", we understand a high-speed mixer equipped in propeller-type agitator and by "low-energy stirrer" a low-speed mixer with a paddle agitator;
- selected mixing time: 2, 6 and 10 minutes for the high-energy stirrer and 5, 10 and 15 minutes for the low-energy stirrer. The times were determined in a preliminary laboratory investigation to obtain time intervals in which colour differences could be detected;
- constant rheological parameters of the glaze slurry;
- exactly similar glaze applications on the ceramic body surface, including the same quantity and thickness of the glaze on the ceramic body surface;
- three different firing curves, which differed as follows:
  - fc-1 – standard curve
  - fc-2 – the same maximum temperature as fc-1 and 10% longer soaking time
  - fc-3 – same firing time as fc-1 and 15^0 higher temperature
- all samples were fired at same time in one firing curve;
- numbers of each set of fired samples were sufficient for statistical control;

The colour of the samples was measured using the spherical Konica Minolta CM 700D spectrophotometer, performing five measurements on the surface of every sample. The colour difference between the prepared samples was determined by mathematical calculations of ΔE_{00} CIDE 2000. The calculation formula is presented below.

$$\Delta E_{00}^{*} = \sqrt{\left(\frac{\Delta L}{S_L}\right)^2 + \left(\frac{\Delta C}{S_C}\right)^2 + \left(\frac{\Delta H}{S_H}\right)^2 + R_T \frac{\Delta C}{S_C} \frac{\Delta H}{S_H}}$$

where:

ΔL′ – is lightness difference; **ΔC′** – is chroma difference; **ΔH′** – is hue difference;

k_L; k_C; k_H – lightness, chroma and hue weighting factors;

S_L – lightness weighting function; **S_C** – chroma weighting function; **S_H** – hue weighting function;

R_T – is a function (the so-called rotation term) that accounts for the interaction between chroma and hue differences in the blue region

For this calculation, the CIE Organization introduced the total scale of colour difference (tonality). This scale was based on the human determination of colour difference in comparison to mathematical calculations. The ΔE scale is shown in Table 1.

ΔE scale	Description
0 < ΔE < 1	usually non-visible difference
1 < ΔE < 2	small differences - require a trained eye
2 < ΔE < 3,5	medium differences - visible to the untrained eye
3,5 < ΔE < 5	sharply visible differences
ΔE > 5	very strong visible differences

Table 1. The ΔE (CIE 1976), limiting value scale for colour differences between two samples of same colour.

Every ΔE is a demonstrated difference in colour between two glaze samples, where only one selected parameter was a variable, in this case the firing conditions. The constant and variable parameters are presented in Figure 2.

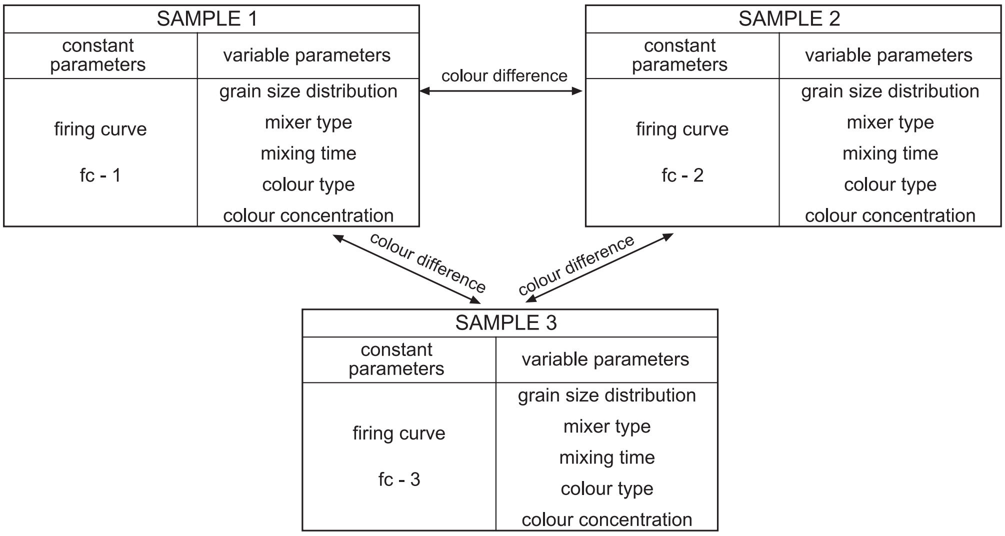

Fig. 2. Constant and variable measured parameters

In this work, the variable parameters were the firing conditions. The colour differences were calculated as a function of the firing curves: that is, 1st curve vs. 2nd curve, 2nd curve vs. 3rd curve and 1st curve vs. 3rd curve. All calculations were carried out for the different pigment types and concentrations, different glaze grain size distributions, and different mixing types and times. The results of the colour difference as a function of the firing curve are presented in Tables 2 to 13, showing the colour differences between the glazed samples, ΔE_{00} CIDE2000 values.

3. RESULTS AND DISCUSSION

The three batches of glaze used in the research were obtained in industrial milling processes. The only difference, except for the type and quantity of the pigment, was the grain size distribution. The results obtained (Fig. 1) show no significant differences in size distributions and could be representative of those that can occur in industrial practice, especially where the primary check point after the milling process depends only on the control of the residue on a 56 μm sieve. The changes in firing conditions could be similar to those in industrial practice, which are sometime used to correct other tile parameters, such as dimensions, planarity or sintering degree. In this sense, the following may be noted, based on the presented ΔE results:

For the dark brown pigment:

- In case of mixing using the low-energy stirrer, in almost all firing conditions a colour difference has been visible. Only in the occurrence of the shortest mixing time and difference in soaking time in the firing condition were invisible tonalities observed.
- In case of application of the low-energy stirrer, the highest tonalities occurred as a function of maximum temperature and temperature and soaking time, apart from colour concentration, mixing time and grain size distribution.
- The highest values of tonalities were above 2,0, which means visible to the untrained eye (all observers).
- The highest tonality occurred most often in the case of the application of the low-energy stirrer and intermediate and fine grain size glazes, irrespective of firing conditions.

For the beige pigment:

- In case of mixing using the high-energy stirrer, in all firing conditions a colour difference has been distinctly visible, independently of mixing time, pigment concentration and grain distribution.
- The highest tonality occurred most often in the case of the application of the high-energy stirrer and intermediate and fine grain size glazes, mainly in the case of the change in maximum temperature and simultaneously temperature and soaking time.
- The highest values of tonalities were above 3,0, which means visible to all observers and close to sharp differences.

4. CONCLUSIONS

The firing process, in the case of coloured glazes (*with dark brown and beige pigments*), significantly influenced the formation of glaze colour differences. This phenomenon was present independently of pigment concentration, glaze grain size distributions, as well type and time of mixing.

In the case of dark brown and beige pigments, both of them were generally quite sensitive to changes in firing conditions, but they were especially sensitive to changes in temperature and soaking time at maximum temperature simultaneously (*firing curve* 3).

The two studied pigments (*dark brown and beige*) demonstrated completely different behaviour with regard to mixing and firing conditions; however, on the basis of the results obtained, further explanation of the reasons for the occurrence of such differences in behaviour is not possible.

The beige pigment was more sensitive to changes in the firing parameters than the dark brown pigment (Tables 2 - 6)

Probably, the majority of the pigments applied in the ceramic industry need similar verification, in regard to their sensitivity concerning glaze grain size distribution, type and time of mixing of the glaze and firing condition.

ACKNOWLEDGEMENTS

This research work was carried out as part of contract of No. 11.11.160.112. Authors especially want to thank their colleagues, Markowi Wójczykowi and Przemysławowi Szwendke for the great contribution in conducting this study.

BIBLIOGRAPHY

[1] Billmeyer, F.W. Jr., Saltzman M. - Principles of Color Technology. Segunda Edición. Chichester, Inglaterra: John Wiley & Sons, 1982

[2] Sharma G. - Digital Color Imaging Handbook; CRC Press LLC, 2003

[3] Stokes M. – Color Management Concepts; Microsoft Corporation, Marzo, 2001

[4] Hunt, R.W.G. - Measuring Colour. Segunda Edición 1991. Chichester, Inglaterra

[5] Ford A., Roberts A. - Colour Space Conversions ; British Broadcasting Corporation, 1998

[6] Johnson G.M., Fairchild M.D. - A Top Down Description of CIE Lab and CIEDE2000; Colour Research and Application, vol 28 (6) Dic. 2003

[7] Sharma G. Wu W., Dalal E.N. – The CIDE 2000 Colour Difference Formula, Implementation Notes, Supplementary Test Data and Mathematical Observations; Colour Research and Application, Feb. 2004.

[8] Del Mar Perez M., Saleh A., Yebra A., Pulgar R. - Study of the Variation between CIELAB ΔE* and CIEDE2000 Color-differences of Resin Composites; Dental Materials journal 26(1) 21-28, 2007

[9] Colour difference formulas – Digital Color Imaging Handbook ed. por Gaurav Sharma, publicado por CRC Press Inc. 2002

[10] Melgosa M. - Color-Difference Formulas; Proceeding of 4th Conference of Balkan Light 2008, Ljubljana Octubre 2008

[11] Luo M.R., Minchew C., Kenyon P., Cui G. - Verification of CIEDE2000 using industrial data. Proceedings of Interim Meeting of the International Color Association, AIC 2004

[12] De Noni A., Paz Rabello V., de Oliviera Modesto C., Hotza D. – Study of colour variation using mixture of pigments based on triaxial diagrams, Proceedings of Qualicer World Congress on Ceramic Tile Quality 2006

[13] Moschik C, Eppich W. – Colour Variation in Screen Printing Ceramics; Ceramic Bulletin Marzo 2003; vol. 82, n 3.

[14] Calculation of colour difference between a reference and a sample colour (Excel ΔE calculation sheet) - Phil Green, Colour Imaging Group,

ΔE CIDE$_{2000}$ colour difference	Coarse glaze grain size (gsd-1)								
	Colour (beige) concentration [%]								
	1	2	3	1	2	3	1	2	3
	High-energy stirrer - mixing time [min]								
	2			6			10		
firing curve 1 vs. firing curve 2	1,267	1,456	1,604	1,999	2,207	2,981	2,227	2,079	2,603
firing curve 2 vs. firing curve 3	2,686	2,616	2,602	1,989	1,928	1,927	1,3	1,252	1,106
firing curve 1 vs. firing curve 3	2,931	2,728	2,369	2,025	2,104	2,523	2,396	2,257	2,757

Table 2. Colour difference ΔE beige coloured, high-energy stirred, coarse grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Intermediate glaze grain size (gsd-2)								
	Colour (beige) concentration [%]								
	1	2	3	1	2	3	1	2	3
	High-energy stirrer - mixing time [min]								
	2			6			10		
firing curve 1 vs. firing curve 2	1,413	1,621	1,768	2,029	2,158	2,814	2,189	2,117	2,334
firing curve 2 vs. firing curve 3	3,002	3,004	2,789	1,9	2,005	2,094	1,259	1,188	0,997
firing curve 1 vs. firing curve 3	3,152	2,927	2,158	2,099	2,073	2,504	2,351	2,208	2,691

Table 3. Colour difference ΔE beige coloured, high-energy stirred, intermediate grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Fine glaze grain size (gsd-3)								
	Colour (beige) concentration [%]								
	1	2	3	1	2	3	1	2	3
	High-energy stirrer - mixing time [min]								
	2			6			10		
firing curve 1 vs. firing curve 2	1,445	1,452	2,014	1,958	2,398	2,744	2,002	2,111	2,397
firing curve 2 vs. firing curve 3	3,099	2,997	2,914	2,064	2,176	2,036	1,252	1,243	1,339
firing curve 1 vs. firing curve 3	3,06	2,74	2,235	1,981	2,167	2,7	2,365	2,345	2,717

Table 4. Colour difference ΔE beige coloured, high-energy stirred, fine grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Coarse glaze grain size (gsd-1)								
	Colour (beige) concentration [%]								
	1	2	3	1	2	3	1	2	3
	Low-energy stirrer - mixing time [min]								
	5			10			15		
firing curve 1 vs. firing curve 2	0,93	0,883	1,017	1,585	2,232	2,18	1,667	2,078	1,981
firing curve 2 vs. firing curve 3	2,699	2,585	2,573	1,694	1,552	2,005	0,841	1,369	1,89
firing curve 1 vs. firing curve 3	2,583	2,777	2,161	2,444	1,773	2,048	1,865	2,639	2,053

Table 5. Colour difference ΔE beige coloured, low-energy stirred, coarse grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Intermediate glaze grain size (gsd-2)								
	Colour (beige) concentration [%]								
	1	2	3	1	2	3	1	2	3
	Low-energy stirrer - mixing time [min]								
	5			10			15		
firing curve 1 vs. firing curve 2	0,884	1,347	1,274	2,621	2,18	2,056	1,839	2,112	1,871
firing curve 2 vs. firing curve 3	2,902	2,95	3,063	2,154	2,001	2,054	1,975	1,188	1,966
firing curve 1 vs. firing curve 3	2,862	3,109	2,482	2,31	1,819	1,683	2,605	2,546	1,988

Table 6. Colour difference ΔE beige coloured, low-energy stirred, intermediate grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Fine glaze grain size (gsd-3)								
	Colour (beige) concentration [%]								
	1	2	3	1	2	3	1	2	3
	High-energy stirrer - mixing time [min]								
	5			10			15		
firing curve 1 vs. firing curve 2	1,199	1,283	1,185	3,095	2,063	1,887	1,8	1,861	1,818
firing curve 2 vs. firing curve 3	2,836	3,16	3,05	2,139	1,948	2,229	1,005	2,058	1,542
firing curve 1 vs. firing curve 3	3,009	2,997	2,55	1,99	1,935	2,103	2,567	2,611	2,017

Table 7. Colour difference ΔE beige coloured, low-energy stirred, fine grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Coarse glaze grain size (gsd-1)								
	Colour (dark brown) concentration [%]								
	1	2	3	1	2	3	1	2	3
	High-energy stirrer - mixing time [min]								
	2			6			10		
firing curve 1 vs. firing curve 2	2,182	1,184	2,295	1,239	1,816	1,635	1,779	1,664	1,197
firing curve 2 vs. firing curve 3	0,887	0,525	0,432	0,825	1,139	0,768	0,602	0,314	0,955
firing curve 1 vs. firing curve 3	1,996	1,615	1,373	1,429	1,464	1,635	1,211	1,664	1,367

Table 8. Colour difference ΔE dark brown coloured, high-energy stirred, coarse grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Intermediate glaze grain size (gsd-2)								
	Colour (dark brown) concentration [%]								
	1	2	3	1	2	3	1	2	3
	High-energy stirrer - mixing time [min]								
	2			6			10		
firing curve 1 vs. firing curve 2	1,842	1,833	2,268	1,231	1,456	1,399	0,928	1,13	0,996
firing curve 2 vs. firing curve 3	0,495	0,509	0,481	0,715	0,898	0,672	0,864	0,653	0,691
firing curve 1 vs. firing curve 3	1,702	1,66	2,234	1,35	1,16	1,915	1,141	1,494	1,536

Table 9. Colour difference ΔE dark brown coloured, high-energy stirred, intermediate grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Fine glaze grain size (gsd-3)								
	Colour (dark brown) concentration [%]								
	1	2	3	1	2	3	1	2	3
	High-energy stirrer - mixing time [min]								
	2			6			10		
firing curve 1 vs. firing curve 2	2,042	1,854	2,17	1,479	1,625	1,386	0,875	1,13	0,886
firing curve 2 vs. firing curve 3	0,58	0,485	0,6	0,758	0,933	0,74	0,965	0,89	0,897
firing curve 1 vs. firing curve 3	1,729	1,651	1,927	1,59	1,187	1,702	1,164	1,46	1,422

Table 10. Colour difference ΔE dark brown coloured, high-energy stirred, fine grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Coarse glaze grain size (gsd-1)								
	Colour (dark brown) concentration [%]								
	1	2	3	1	2	3	1	2	3
	Low-energy stirrer - mixing time [min]								
	5			10			15		
firing curve 1 vs. firing curve 2	1,898	1,631	1,89	1,585	2,232	2,18	1,667	2,078	1,981
firing curve 2 vs. firing curve 3	0,326	0,303	0,281	1,694	1,552	2,005	0,841	1,369	1,89
firing curve 1 vs. firing curve 3	2,01	1,458	1,685	2,444	1,773	2,048	1,865	2,639	2,053

Table 11. Colour difference ΔE dark brown coloured, low-energy stirred, coarse grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Intermediate glaze grain size (gsd-2)								
	Colour (dark brown) concentration [%]								
	1	2	3	1	2	3	1	2	3
	Low-energy stirrer - mixing time [min]								
	5			10			15		
firing curve 1 vs. firing curve 2	2,175	1,574	1,638	2,621	2,18	2,056	1,839	2,112	1,871
firing curve 2 vs. firing curve 3	0,544	0,427	0,453	2,154	2,001	2,054	1,975	1,188	1,966
firing curve 1 vs. firing curve 3	1,851	1,468	1,392	2,31	1,819	1,683	2,605	2,546	1,988

Table 12. Colour difference ΔE dark brown coloured, low-energy stirred, intermediate grain size glaze as a function of firing conditions.

ΔE CIDE$_{2000}$ colour difference	Fine glaze grain size (gsd-3)								
	Colour (dark brown) concentration [%]								
	1	2	3	1	2	3	1	2	3
	Low-energy stirrer - mixing time [min]								
	5			10			15		
firing curve 1 vs. firing curve 2	2,062	1,556	1,831	3,095	2,063	1,887	1,8	1,861	1,818
firing curve 2 vs. firing curve 3	0,644	0,294	0,487	2,139	1,948	2,229	1,005	2,058	1,542
firing curve 1 vs. firing curve 3	1,767	1,477	1,549	1,99	1,935	2,103	2,567	2,611	2,017

Table 13 Colour difference ΔE dark brown coloured, low-energy stirred, fine grain size glaze as a function of firing conditions.