STUDY OF THE MIXTURES AND PROCESSING CONDITIONS CAUSING VARIATIONS IN THE HUE OF VANADIUM BLUE PIGMENT

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ABSTRACT

A major and very common problem in the ceramic tile industry is variations in hue from one tile to another. These variations not only impair the product's appearance but also increase stock management costs, and are therefore highly prejudicial to product competitiveness. The causal factors of variations in hue can be classified into three groups: a) factors involved in the pigment preparation process; b) those relating to pigment application conditions; and c) those associated with the pigments' physical and chemical characteristics. Ceramic pigments, particularly (V,Zr)SiO_4 turquoise blue, are a class of materials widely employed in the worldwide ceramic industry, of which the manufacture of ceramic tiles represents a considerable percentage. These products are manufactured according to "recipes" having several mutually competing variables [1] that define the product's final results. The use of statistical tools for process control, development and improvement is therefore increasingly required so that the optimal point of maximum quality can be achieved to render the product competitive, considering that the lower the waste and the higher the yield from reaction processes in the solid state, the higher the final profits. From the environmental standpoint, this optimization is also significant, according to Llusar, M. [2], since it is aimed at minimizing solid, liquid and gaseous wastes. This work employed tools for statistically designing experiments to study some mixture and process variables directly affecting the development of the colour of zircon and vanadium blue pigment produced industrially, using a CIELab colorimeter, compared with a standard (target) industrial pigment. The experiment was divided into three steps: (1) A list was drawn up of almost fifteen aspects of processing conditions and proportions of raw materials currently in use, which were considered the major factors contributing to pigment efficiency. (2) Based on previous experience, some factors were then eliminated from a list of what were considered the most important process variables requiring analysis. (3) A screening experiment was conducted to identify the process-related factors contributing most strongly to decreasing hue variations, thereby reducing the number of significant factors involved in these variations. Our findings, which are easily applicable to industrial processing, reveal the factors that most contribute to reducing variations in hue.

1. MATERIALS AND METHODS

The factorial planning technique was tested in the production process of $(V,Zr)SiO_4$ turquoise blue ceramic pigment. The factors of interest tested here were: Mixing Methods (M) – 1) Hammer milling and Hammer milling followed by ball milling; fineness of the quartz (Q) – #200 and #400; Threshold firing temperature (T) – 900 and 1100°C; Soaking time at maximum temperature (P) – 2 and 5 hours. The factorial planning used was 2^4, in which four variables (M, Q, T, and P) were defined at two levels. The schematic diagram of the experiment (Figure 1) illustrates the calculations made to estimate the effects of each variable. The detailed methodology, as well as the calculation of the effects of each variable (M, P, T and P) and of their interactions (MQ, MP, QT, QP, TP, MQT, MQP, MTP, QTP and MQTP) is described by Montgomery[3]. A statistical program was used which, based on the variables and conditions, indicates the necessary experiments and the random order in which to carry them out (Table I). Note that Table I shows a Standard Order and a Run Order, which indicate the sequence taking into account, respectively, the levels of the experimental variables and the random sequence to be followed. The samples were weighed following the proportion adopted in industrial production, varying only quartz fineness. After weighing, the samples were mixed by two different methods: 1st – Ground once in a hammer mill, and 2nd – ground once in the hammer mill and another 15 minutes in a laboratory ball mill. The next step consisted of calcining approximately 10g of the samples in closed porcelain crucibles, varying the soaking times (2 and 5 hours) and using two temperatures (900 and 1100°C). After they were calcined, the pigments were ground with water in a zirconium ball mill containing 50% solids and 8% NaOH for exactly 5 minutes, followed by washing in three 1-litre rinses and subsequent drying. After the samples were completely dry, they were pounded with a pestle in a mortar to ready them for the application. The powdered samples were mixed with 5% pigment in a standard clear glaze and a 0.5 mm layer applied on the prepared surfaces of BIIb ceramic tiles. The pieces were carefully arranged in the central row of an industrial furnace in order to minimize temperature gradients and fired at 1130°C. The colour was then analyzed using a MINOLTA cm 2500d spectrophotometer with D65 illumination at 10°.

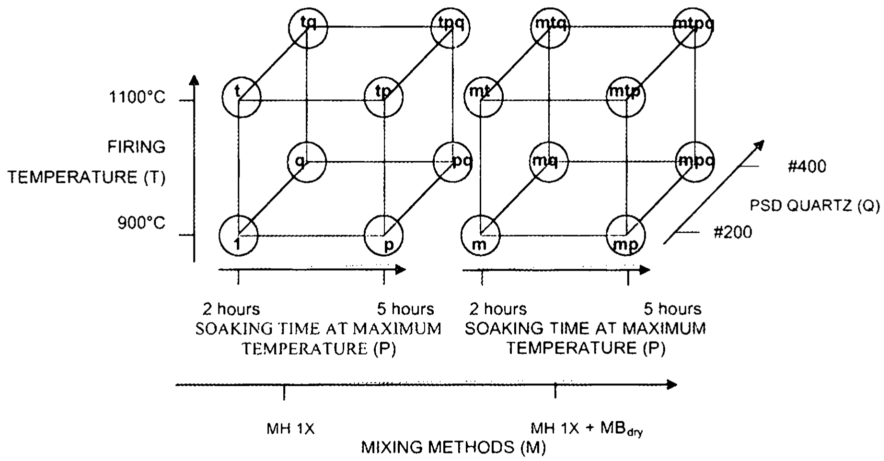

Figure 1. Schematic diagram of the experiments conducted

Std Order	Run Order	Mixture	Quartz-SiO_2 (mesh)	Temperature (°C)	Time (h)	ΔE
3	1	Hammer	#400	900	2	4.8831475
16	2	Hammer + balls	#400	1100	5	12.559198
8	3	Hammer + balls	#400	1100	2	12.121533
6	4	Hammer + balls	#200	1100	2	9.5850531
12	5	Hammer + balls	#400	900	5	5.9019182
7	6	Hammer	#400	1100	2	14.693243
14	7	Hammer + balls	#200	1100	5	14.477468
1	8	Hammer	#200	900	2	8.7777336
5	9	Hammer	#200	1100	2	6.8223682
11	10	Hammer	#400	900	5	23.006648
15	11	Hammer	#400	1100	5	14.859578
10	12	Hammer + balls	#200	900	5	4.9472246
2	13	Hammer + balls	#200	900	2	5.1687316
4	14	Hammer + balls	#400	900	2	7.4615223
9	15	Hammer	#200	900	5	10.158266
13	16	Hammer	#200	1100	5	26.11266

Table 1. Experiments carried out with the precursor mixtures and ΔE variation

3. RESULTS AND DISCUSSION

The above methodology led to the results given in Table 2, below, which shows the effects of each factor and interaction. The more negative the numerical value, the greater its contribution toward reducing variations in hue. An analysis of the values indicates that the improvement in the mixing method (M) achieved by adding the ball milling step contributed the most to the final colour of the ceramic pigment. In contrast, the reduction in the quartz particle size from #200 to #400 mesh led to a negative effect, albeit not as marked as the increase in temperature (from 900 to 1100°C) and in time (from 2 to 5 hours). However, joint effects – the so-called interactions – can contribute in the same way as isolated factors. Thus, the result of the association between the factors mixing method (M) and threshold time (P) is the M*P point, acting jointly and generating effects similar to the improvement of the mixing method. This is extremely important in the production process since, industrially, it is easier to adjust a single variable rather than two or more to obtain an improvement. That is why the finding presented here – that a simple adjustment of the mixing method leads to results which would otherwise only be obtained by varying more than one factor – is extremely advantageous. The colorimetric results listed in Table 1 show a high ΔE value, indicating that the pigments displayed significant variations in hue. However, it should be noted that the pigment used as the standard was high quality, and that the purpose of this work was to identify the influence of raw material and processing on the reduction of ΔE; hence, the comparison between them was more important than the absolute value.

FACTORS AND INTERACTIONS	EFFECTS
M	-4.636
Q	1.18
T	5.116
P	5.314
M*Q	-0.213
M*T	1.2
M*P	-4.426
Q*T	-1.871
Q*P	-1.022
T*P	0.883
M*Q*T	1.213
M*Q*P	-0.426
M*T*P	0.895
Q*T*P	-4.873
M*Q*T*P	4.094

Table 2. Effect of the factors and the interactions on the variations in hue (ΔE)

4. CONCLUSIONS

The results of these experiments enabled us to identify the most favourable and the most detrimental factors that influence the reduction of variations in hue (ΔE). In other words, greater emphasis should be placed on the method when optimizing the synthesis of this pigment.

5. ACKNOWLEDGEMENTS

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