DESIGN OF EXPERIMENTS WITH MIXTURE VARIABLES APPLIED IN THE FORMULATION OF BLUE CERAMIC PIGMENT (V-ZRSIO$_4$)

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ABSTRACT

Pigments play a crucial role in the manufacture of ceramic tiles. Today, the process most commonly used in the industrial synthesis of these pigments is the solid state reaction of oxides and other raw materials. Although this process has long been utilized, the role of the several variables involved is as yet little understood, so most manufacturers still work with formulas without a real understanding of the process. Under such conditions, if any given raw material is unavailable or too costly and must therefore be replaced, or even if the characteristics of a raw material have changed, the formula may no longer work adequately, thus posing a serious problem for the manufacturer.

In this context, the present work purported to apply the design of experiments (DOE)[1,2,3] [1,2,3] tool to mixtures in order to study the synthesis of turquoise blue ceramic pigment V-ZrSiO$_4$. To this end, the variable to be studied was the proportion of ZrO$_2$, SiO$_2$, V$_2$O$_5$ precursors and mineralizers, for which the necessary combination was determined for a linear model with a central point, using statistical software. The control parameters were the colorimetric readings of the tile samples, which were prepared under standard conditions simulating the real setup and were fired simultaneously in an industrial kiln. The processing conditions were standardized to allow for a comparative evaluation of the results, which were treated with statistical software. A linear polynomial was then modeled with an inverse term that relates the measured property (ΔE) as a function of the contents of the three different raw materials used in the desired pigment. This simple procedure enhanced control over the manufacturing procedure, facilitating the evaluation of substitute raw materials and providing information regarding the consequences of changing the proportion of raw materials.

1. MATERIALS AND METHODS

The experimental stage began with a listing of the chemical and production characteristics of this type of pigment, based on a review of the literature[4,5,6,7], contacts with manufacturers, and prior analyses of industrial pigments. The work intervals shown in Table 1 were then defined based on this information.

PRECURSOR	LOWER LIMIT (wt%)	UPPER LIMIT (wt%)
ZrO_2	43.2	53.3
SiO_2	21.6	26.65
V_2O_5	1.8	8.2
Mineralizer	18	28

Table 1. Sampling interval of the precursors

The formulations were defined by statistical software (Minitab Corporation's *Minitab* 13.30) with random sequencing, seeking to adjust a first order polynomial (linear model), with the presence of a composition at the central point of the sampling space, with replications. Starting from the definition of the sampling space, the statistical program generates the formulations needed to represent it. These formulations are shown in Table 2. Note that this table presents the variables in a pattern of increasing order (Standard Order) and in random order (Run Order) to be followed.

STANDARD ORDER	RUN ORDER	ZrO_2 (%)	SiO_2 (%)	V_2O_5 (%)	MINERALIZER (%)
3	1	43.2	21.6	8.2	27.0
13	2	48.1	24.1	4.9	22.9
7	3	43.6	26.7	1.8	28.0
5	4	48.6	21.6	1.8	28.0
10	5	53.3	21.6	7.1	18.0
6	6	43.2	21.6	7.2	28.0
11	7	47.2	26.7	8.2	18.0
1	8	53.3	21.6	1.8	23.3
4	9	43.2	26.7	8.2	22.0
9	10	52.2	21.6	8.2	18.0
12	11	53.3	26.7	2.1	18.0
8	12	43.2	26.7	2.2	28.0
2	13	53.3	26.7	1.8	18.3

Table 2. Compositions of the raw materials tested, in percentage of mass

Based on the data in Table 2, the pigments were synthesized, the compositions weighed on an analytical scale with a confidence level of ±0,001g, dry mixed in a ball mill, and calcined at 900°C for 2 hours in a covered crucible. To remove the soluble salts and possible unreacted precursors, basic leaching was performed using 8% of NaOH. The pigments were washed in 3 liters of water, broken up with a pestle and subjected to the application phase. Using a mechanical mixer, the pigments were incorporated into standard transparent enamel (5% dry base) and a 0.5 mm layer applied with a binil on engobed BIIb ceramic floor tiles, following a template placed beside them. The tiles were then fired in an industrial furnace in a 30-min cycle at a maximum

temperature of 1140°C. The samples' chromatic coordinates within the CIELab space were characterized, comparing them to the template using a Minolta 2600d diffuse reflectance spectrophotometer with D65 illumination at 10°. The results were treated in order to calculate the total chromatic variation, ΔE

2. RESULTS AND DISCUSSION

The colorimetric results were treated using a chart to calculate the total chromatic variation (ΔE), whose results are shown in Table 3.

FORMULATION	ZrO_2/SiO_2 (%)	V_2O_5 (%)	MINERALIZER (%)	ΔE
1	2.00	8	27	2.61
2	1.99	5	23	2.29
3	1.63	2	28	41.99
4	2.25	2	28	43.69
5	2.47	7	18	26.46
6	2.00	7	28	6.31
7	1.77	8	18	8.38
8	2.47	2	23	43.18
9	1.62	8	22	4.41
10	2.42	8	18	2.15
11	2.00	2	18	43.55
12	1.62	2	28	42.44
13	2.00	2	18	41.8

Table 3. Colorimetric results and raw materials used, in percentage of mass

An analysis of the results indicates that some of the pigments were promising, with a relatively low ΔE. Formulations 1, 2 and 10 showed the best performance. It should be noted that the pigment used as standard is of excellent origin and underwent to process of comminution, called micronization, which produces small particles and a narrow distribution. This process cannot be reproduced in the laboratory, and was therefore incorporated as a deviation of the experimental work. Therefore, the results presented here were considered satisfactory and consistent, although only a semi-industrial application could isolate the external factors that cannot be controlled in the laboratory. Formulation 2 showed a relation that is highly scrutinized by the industry, i.e., cost. This formulation contains 5% dopant rather than the 8% in formulations 1 and 10. The 3% reduction of this raw material greatly reduces the product's end cost, since vanadium pentoxide is the most expensive raw material.

STATISTICAL PARAMETER	RESULTS FOR THE CONSEQUENT INVERSE TERMS			
	1/ %ZrO_2	1/ %SiO_2	1/% V_2O_5	1/ %Mineral.
R^2_{aj}	80.28%	92.71%	81.90%	82.35%
Regression (p)	0.001	0.000	0.001	0.001
Linear (p)	0.001	0.000	0.868	0.001
Inverse Term (p)	0.219	0.003	0.142	0.126

Table 4. Statistical results for a linear function with the various inverse terms tested

The results were treated statistically to adjust the best polynomial representing the experimental points obtained; several regression methods were tested, from direct linear models to linear models with inverse and quadratic terms. The modeling for the experimental points using $\%SiO_2$ as the inverse term proved satisfactory, with an R^2_{aj} of 92.71% and all the ***p*** parameters lower than 0.01 (as shown at Table 4 and as the polynomial at equation A). The other attempts to model a polynomial using inverse terms produced unsuitable results, with at least one ***p*** value exceeding tolerance and an R^2_{aj} below 90%.

(A)

We were therefore able to represent the analyzed region graphically with a good adjustment, with the desired contour lines to allow for work on the formulations, as in a phase diagram. As mentioned earlier, the region in the space represented by 4 variables is a regular tetrahedron that cannot be used for analysis, so cross-sections were cut in three positions of this tetrahedron, corresponding to the regions of 18, 23 and 28% of mineralizer.

The diagram in Figure 1 is highly informative, showing the region in which one obtains each variation in tone, as well as the proportion of raw materials required to reach the result indicated in the figure.

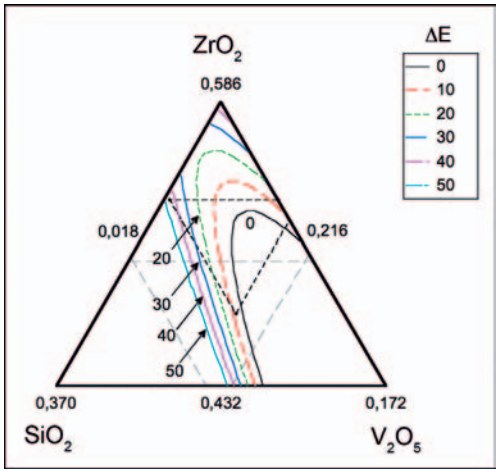

Figure 1. Contour lines for the composition containing 18% of mineralizer

When producing a ceramic pigment, the objective is for it to show ΔE tending to zero, which represents the absence of chromatic variations in comparison with a template or standard. Note that the contour line with zero ΔE is well defined and that it shifts toward an increase in dopant (V_2O_5) content, indicating its importance in the product's final colour.

In principle, as a working tool, all the compositions developed at the triple points in the diagram (SiO_2, ZrO_2 and V_2O_5) above the line where ΔE is equal to zero, with 18% of mineralizer, processed as shown in the flowchart of Figure 1, should have colorimetric parameters close to those of the standard, with a representativeness of 92.71%. This provides compositional flexibility, allowing one to find the compositions presenting the greatest industrial advantages.

Figure 2 shows a contour line with ΔE tending to zero, which is better developed than in the previous case, allowing for an increase in the range of formulations. This

is advantageous for the manufacturer, since it gives him greater flexibility in the proportions of raw materials applied in the development of a pigment.

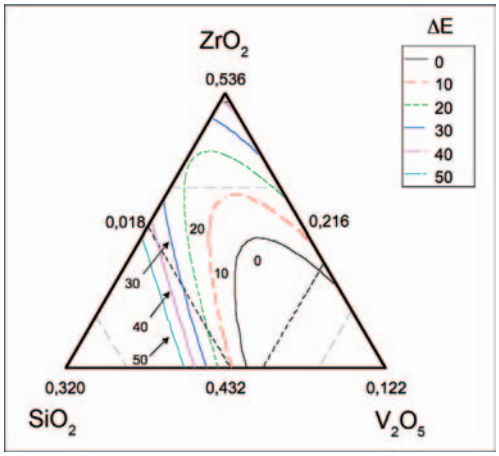

Figure 2. Contour line for the composition containing 23% of mineralizer

Note that, with 28% of mineralizer (Figure 3), the contour line with ΔE tending to zero diminishes considerably. This is a negative factor in the development of new and more feasible formulations, for it restricts the range of compositional variations that would generate pigments with qualities similar to those of the standard.

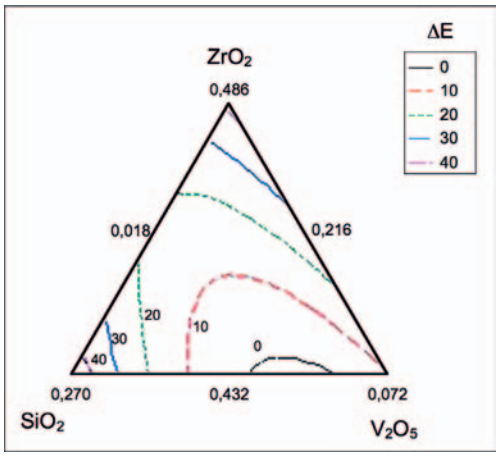

Figure 3. Contour lines for the composition containing 28% of mineralizer

3. CONCLUSIONS

The results of our experiments led us to the following conclusions:

- The mixed design of experiments technique allowed us to analyze a sampling space with a great deal of information in only 13 experiments.
- The pigments developed with this technique proved promising.
- We were able to model a linear equation with a high degree of adjustment and with high statistical significance, correlating the proportions of raw materials and the desired property (ΔE=0).

- The triaxial diagrams provide a large amount of information, proving to be an extremely useful tool for studying the development of new, more viable formulations for the industrial sector.

4. ACKNOWLEDGEMENTS

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