STATISTICAL INVESTIGATION AND OPTIMISATION OF FRIT COMPOSITIONS CONTAINING B_2O_3 FOR "MONOPOROSA" WALL TILE GLAZES

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1. INTRODUCTION

The introduction of fast-firing technology in mono-canal roller kilns has created dramatic changes in their production cycle and equipment. The advantages of this new technology are the following: energy saving, the possibility of tile size variation, automated production, fast-firing, use of cheaper raw materials and high production quality [1]. The development of the manufacture of facing tiles and the variety of ranges available are closely connected with the type, design and quality of the glazes used. The glazes used nowadays are multicomponent, high-melting or low-melting glasses with a varied composition, containing mainly SiO_2 and B_2O_3. B_2O_3 easily forms a glass in which three oxygen ions are coordinated with every boron ion. These three-cornered groups form a continuous spatial lattice. In the glazes, B_2O_3 reduces the softening and melting temperatures, lowers surface tension and improves their mechanical and thermal properties [2,3]. On the other hand, B_2O_3 considerably influences the aesthetic characteristics of the coating because of the special optical effects created by its inclusion [4]. Faience glazes are fired in the temperature range from 900 to 1280°C. The bright glaze coatings are then added and can be matted with one or more crystal phases. During recent years, there has been an increasing use of zirconium compounds in glaze coatings.

The aim of the present work has been to investigate the functional dependence of white borate cover frit properties on the quantities of raw material involved in its manufacture using a standard experimental procedure, and to find the optimum frit composition. To develop this procedure, however, it is necessary to know the glaze formation region.

[1] N. Tozzi, *Smalti Ceramici Consideration Teoriche e Practiche* (Gruppo Editionale Faenza Editrice, Faenza, 1992).

[2] S. Stefanov and S. Batchvarov, *Smalti Ceramici* (Gruppo Editionale Faenza Editrice, Faenza, 1994).

[3] R. Smith, J. *Non-Cryst. Solids* 84 (1986), 421.

[4] S. Djambazov, N. Nedeltchev, Y. Dimitriev, Y. Ivanova and A. Yoleva, *In: Borates Glassses, Crystals and Melts*, Eds A.C. Wright, S.A. Feller and A.C. Hannon (Soc. Glass. Technol., Shefheld, 1997), pp. 1-7.

2. EXPERIMENTAL

2.1. RAW MATERIALS

In order to carry out this investigation, the following raw materials were used for preparing the glazes:

(i) Technical products with purity above 98%: sodium nitrate, zinc oxide, boric acid, borax;

(ii) Natural raw materials: feldspar, zircon, limestone, kaolin, dolomite and quartz sand.

2.2. DESIGN OF EXPERIMENTAL PROCEDURE

The experimental design was performed using the McLean and Anderson method [5]. Six components were varied. The basic frit composition is given in weight percent in Table 1.

Nº	*Raw material*	*Percentage*	*Varied and constant components*
1.	Feldspar	25%	constant
2.	Boric acid	6%	constant
3.	Borax	5-20%	X1
4.	Limestone	5-15%	X2
5.	Zircon	8-15%	X3
6.	Zinc oxide	0-10%	X4
7.	Quartz sand	30%	constant
8.	Sodium nitrate	1-7%	X5
9.	Kaolin	0-8%	X6
10.	Dolomite	5%	constant
	Total sum	100%	

Table 1. *Basic Frit Compositions .*

The total percentage of the variable components was constant at 34% and their range is indicated in the table. An exact and sequential optimised procedure was established for the experimental runs.

2.3. EXPERIMENTAL PROCEDURE

2.3.1. Preparation of the test samples

Thirty experimental runs were performed under industrial conditions, to yield 30 frit compositions for ceramic "monoporosa" wall tiles. For each run, 5 kg of frit was melted in a gas-fired kiln at 1450°C for 2 hours. The frits obtained were granulated by

[5] S. Stoyanov, *Optimisation of technological objects* (Technika, Sofia, 1983).
[6] I. Wuchkov and Ch. Yonchev, *Design and experimental analysis of mixture properties investigations* (Technika, Sofia, 1979).

quenching in water. After wet grinding the frits together with the additives in fast ball mills, aqueous suspensions were obtained, which represent the glaze slips. For all of the glazes investigated, enriched kaolin was used in a quantity of 8%, as a grinding additive. The glazes were ground to pass a 10,000 mesh screen. The glaze application was performed over 250 x 200 mm green-pressed tiles by spraying and the tiles were fired at 1050°C in a roller kiln for 62 min.

2.3.2. Determination of glaze properties

The following frit properties were investigated: viscosity, thermal expansion coefficient, softening temperature and glass transformation temperature. The comparison of frit viscosity in the melting range was carried out at a temperature of 1100°C by measuring the frit flow length in unglazed ceramic sloping grooves 90 mm in length, 12 mm in width, 4 in depth. The determination of the thermal expansion coefficient, softening temperature and glass transformation temperature was performed using a Hench apparatus. The properties of the resulting glaze – brightness, flowability and covering – were determined by expert opinion and glaze whiteness of the tiles was measured with an apparatus, produced by Carl Zeiss – Jena. High chemical purity MgO was used as a standard.

2.3.3. Processing of data and construction of composition-property diagrams

The experimental data have been processed by regression analysis. Second order polynomial models were employed, using the DESIGN EXPERT computer program. Models were used to perform a multicriterion optimisation based on a desirability function. The generalized desirability coefficient was 0.6991. The optimum composition is, however, only appropriate for the given factory, for which the experimental design and mathematical models were worked out. To obtain the composition-property diagrams, the components of the optimum frit composition were varied such that three of them remained at their optimum values and the other three were varied within their permissible limits.

3. RESULTS

The optimum frit composition in a compromise region of glaze - formation was been found to be:

BORAX	8.186 %
LIMESTONE	5.000 %
ZIRCON	14.230 %
ZINC OXIDE	3.373 %
SODIUM NITRATE	1.052 %
KAOLIN	2.157 %

The influence of the raw material components on the whiteness of the glaze surface has been investigated using the above model. Twenty composition - property diagrams were constructed. For example, three diagrams are shown in Figs.1-3, which present the influence of borax, zircon and sodium nitrate on the whiteness of "monoporosa" wall tile glazes.

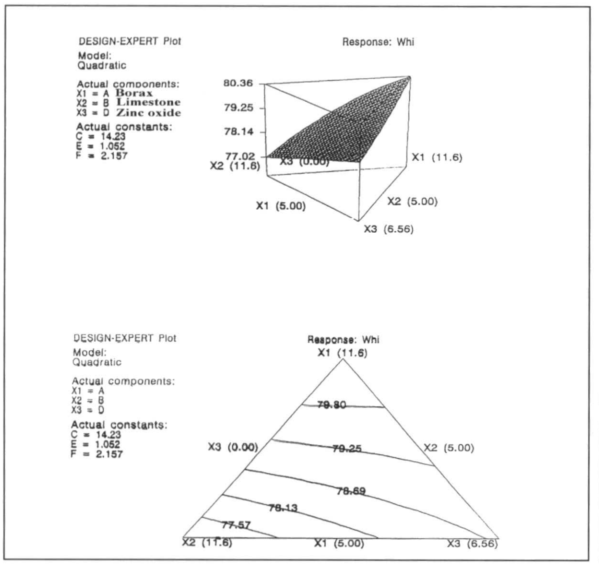

Figure 1. Composition-property diagram showing the influence of zircon on the whiteness of "monoporosa" wall tile glazes (A - borax, B - limestone, D - zinc oxide).

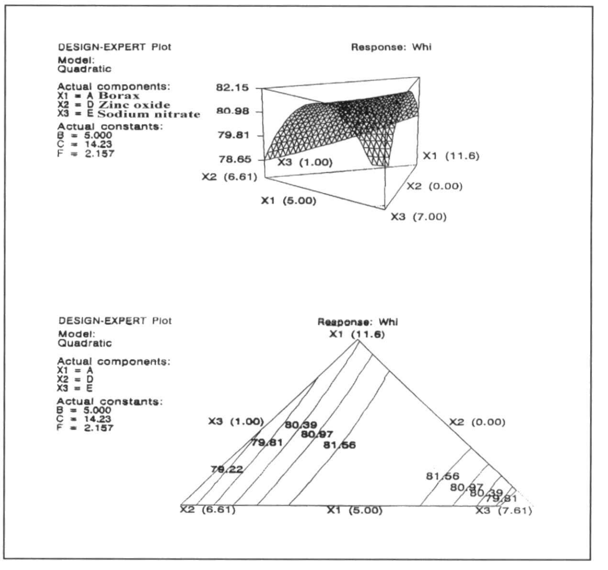

Figure 2. Composition-property diagram showing the influence of zircon on the whiteness of "monoporosa" wall tile glazes (A - borax, B - zinc oxide, D - sodium nitrate).

From these figures, it can be seen that:

- Whiteness increases with increasing borax quantity in the frit.
- The zircon content and the zinc oxide content strongly influence whiteness.
- The maximum whiteness values are obtained at a minimum limestone content of 5%.
- The optimum quantity of sodium nitrate in the frit is 3-5%.
- The presence of kaolin in the frit has a negative effect on glaze whiteness.

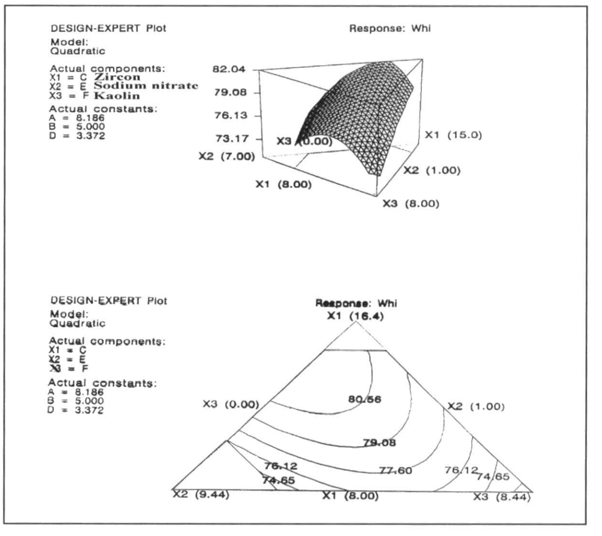

Figure 3. Composition-property diagram showing the influence of sodium nitrate on the whiteness of "monoporosa" wall tile glazes (A - zircon, B - sodium nitrate, D - kaolin).

4. CONCLUSION

Multicriterion optimisation based on a desirability function has been performed. The optimum frit composition for "monoporosa" wall tile glazes in a compromise region of glaze-formation was developed The influence of the raw material components on the glaze surface properties was established.