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The study of non-noxious ceramic colorants based on bismuth oxide

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The ceramics industry is increased developing worldwide; the fabrication of ceramic products in ever higher volume and scale is not only the result of the increase of quantitative and quality requirements for such products, in various usage fields, but also of the possibility of replacement of some materials, in higher performance conditions. The work aimed at working out-ceramic frits and colourants that, along with a good harmony with the ceramic mass, meet the non-toxicity criterion, through the substitution of lead oxide with bismuth oxide.The used methods of study and characterization were: thermal derivatography, X-ray diffractometry, thermal microscopy, thermal expansion, optical microscopy and colorimetry.

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1. Introduction

Original experimental studies based on actual issues of labor protection, health and natural environment, regarding the exclusion of endangerment of human health by yielding the noxious substances from plates and dishes, have been worked out [1].

Lead oxide has an important role in production of good quality ceramic coatings has been. Despite its usage in ceramics from several centuries, today there is a tendency of rejecting it and replacement with other concurrent raw materials for avoiding the endangerment of living beings' health by the lead solubilized in food or breathed in during fabrication process. Its positive effect verified during time and the negative effects brought by its solubilization and toxic attack were hung in balance [2,3]].

This study has as objectives:

- rigorously fitting the condition of yielding the noxious elements (lead), according to world's legit limits for national and export destined production of plates and dishes [4];
- the compatibility of flux with an as large as possible number of oxidic compositions working as a ceramic pigment; the flux has to sustain, even allow the development of pigment's characteristic color.

2. Experiments

A frit in which bismuth oxide replaced lead oxide, was elaborated and studied in detail regarding the thermal and physico-chemical behavior and the coloring properties as well; by using a proposed new frit, a large scale of colorants for the phosphatic porcelain glazes was synthesized [5].

The comparative study of lead oxide and bismuth oxide frits has put in evidence their parallel behavior in the 20-1300^{0}C temperature range. Although at low temperatures (500^{0}C-700^{0}C) there is some difference between the reactivity of those two oxides, the plumbous one providing a higher chemical aggressivity, having a higher capacity of dissolution of quartz in comparison to bismuth, at higher temperatures (1000^{0}C-1300^{0}C), found at elaboration of synthetic fluxes for colorants, the processes are similar, with same outcome: transparent, glossy and weakly colored glass, able to act like a vitreous matrix in ceramic colorants.

The masses tested as ceramic colors were made of fluxes *a* (prepared with lead oxide) and *b* (prepared with bismuth oxide) in 80-85% proportions and of industrial pigments, in 15-20% proportions. The red and yellow pigments from the formula of cadmium and selenium double sulphide, with high coloring power, are the only ones taken in concentrations lower than 20%. 24 pigments were tested and tried in the two frits: blue, red, yellow, brown, green, black and white pigments.

The experiments were performed in perfect parallelism for the two frits. All technological parameters were maintained constant, so that the results not to be influenced by any of several factors that could affect the obtained color.

The study aimed also at the investigation of some aspects with regard to firing behavior of ceramic colorants, in order to recommend control and study methods that are more secure and less subjective than those applied until now.

3. Results

The comparative studies for one of studied series on blue colorants are presented, by using spinelic blue colorants pigment (zinc and cobalt aluminates).

- The sample *1a* – ceramic colorant made of lead oxide frit
- The sample *1b* – ceramic colorant made of bismuth oxide frit

From microscopic point of view (figures 1,2) the two colorants show vitreous-crystalline structures, with lightly porous textures. The index of refraction of the glass that stands for the vitreous matrix of the colorant is uniform and identical for both frits. The vitreous mass is colorless. These two characteristics indicate that the pigments have not been resolved in the flux, so the flux discharged its duty of dispersing medium and binder for the glaze. The pigment's dispersion in the glass mass is relatively uniform for both colorants.

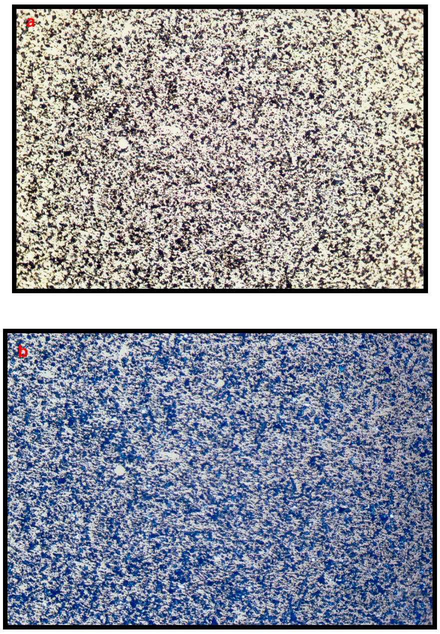

Fig. 1. Microscopic image of sample 1a in polarized light (1 N; 100×); b. (N+; 100×).

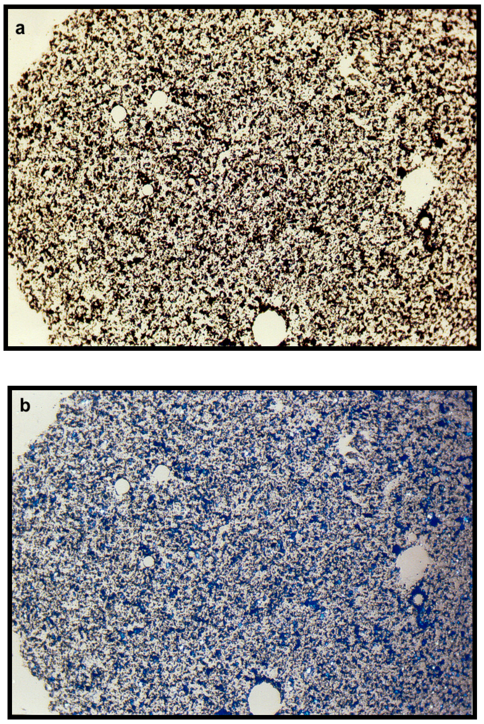

Fig. 2. Microscopic image of sample 1b in polarized light(1 N; 100×); b. (N+; 100×).

The diffractograms obtained on 1a for lead (figure 3) respectively 1b for bismuth (figure 4), show the same diffraction lines corresponding to spinelic structure.

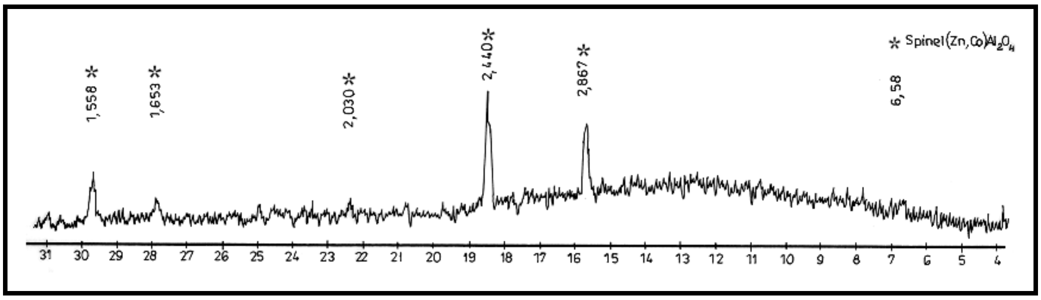

Fig. 3. *X-ray diffraction spectrum of colorant 1a*

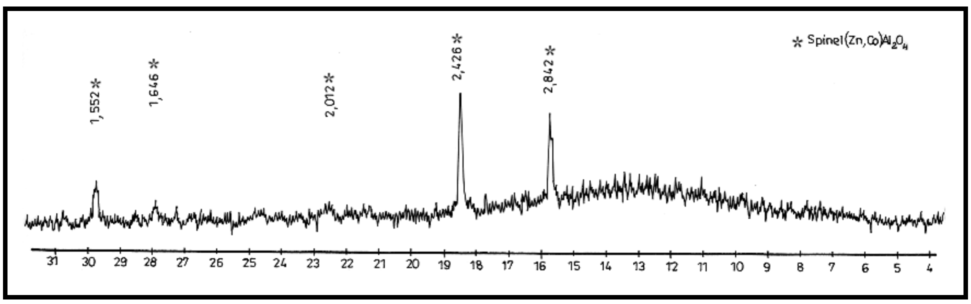

Fig. 4. X-ray diffraction spectrum of colorant 1b.

The comparative studies for one of studied series on red colorants are presented, by using red pigment (cadmium and selenium double sulphide)

- Sample *5a* – colorant made of lead oxide frit
- Sample *5b* – colorant made of bismuth oxide frit

From microscopic point of view, the structure of colorant 5a (figure 5 a,b) is vitreous-crystalline, having a porous texture. The porosity is high, being ~ 40%. The glass is colorless and homogeneous. The index of refraction is about 1.55. The pigment is made of small isometric grains, with very high index of refraction (~ 2.5); this is the reason why it looks opaque. At crossed nicols, anisotropy is observed, the red color being provided by internal reflexions.

The structure of colorant 5b (figure 6 a, b) is vitreous-crystalline, having a porous texture. The porosity is enough high, reaching 20%. The glass is homogeneous, transparent, colorless, having N~1.55. At this sample there is a big difference between the glass' index of refraction and the pigment's (N~ 2.5) and pigment's density is much higher than previous sample's (5a) because of the separation of metallic Bi. At crossed nicols, the color is brown, due to mixture of cadmium and selenium double sulphide and bismuth.

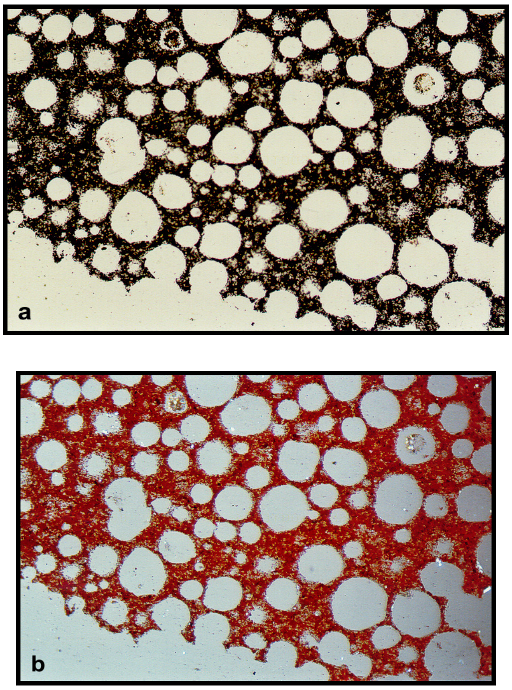

Fig. 5. Microscopic image of sample5a in polarized light a.(1 N; 100×); b. (N+; 100×)

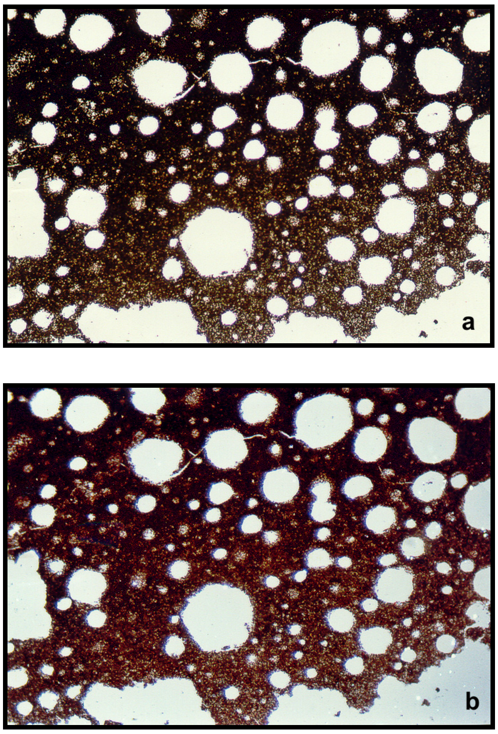

Fig. 6. Microscopic image of sample5b in polarized light a. (1 N; 100×); b. (N+; 100×)

The X-ray diffractogram made on the pigment. puts in evidence the complete spectrum of greenockite (CdS-the hexagonal system), with a kind of higher d values, due to participation of selenium in the structure. The lead-based colorant shows a spectrum corresponding to greenockite (figure 7). The intensity of lines is diminished due to decrease of content in the crystalline substance. The bismuth based colorant (figure 8) shows a diffractogram with lines corresponding to greenockite and metallic bismuth (the trigonal system).

In conclusion, it may state that the lead oxide frit is convenient for red colorants. The sulphide pigments have partially reduced bismuth oxide at the metal, the color being affected by superposition of the brown-grey effect of its particles on the brightly intense red of cadmium and selenium double sulphide.

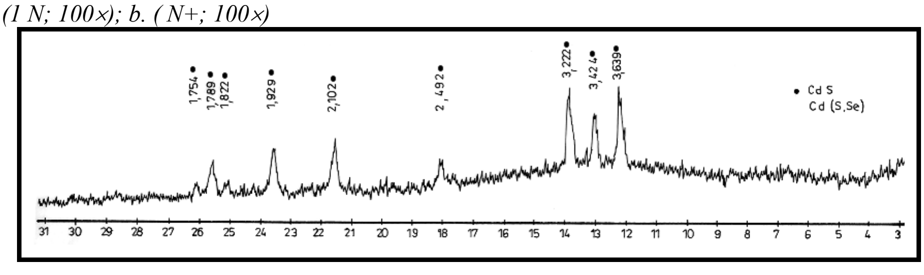

Fig. 7. X-ray diffraction spectrum of colorant 5a

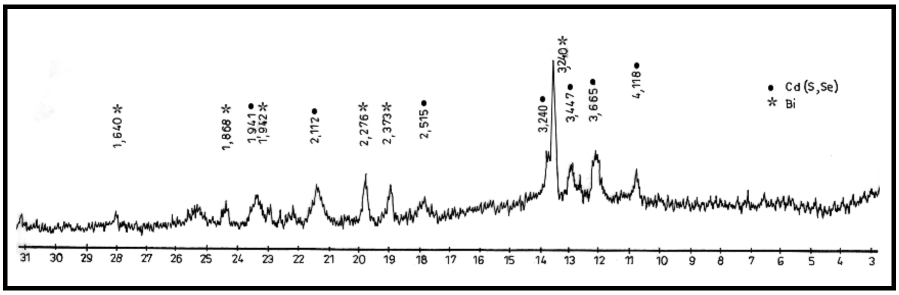

Fig. 8. X-ray diffraction spectrum of colorant 5b

The studied bismuth oxide frit is not compatible with orange and red pigments in the composition placed in cadmium and selenium double sulphide chemical system and probably the partial reduction of metallic oxide is responsible for destroying some colorants from this scale, during firing of decorations.

The determination of thermal behavior of examined colors puts in evidence the similitude of the two colorants types: with lead oxide-based frits, respectively bismuth oxide-based frits; the ceramic colors are thermally stable. The melting temperatures are almost the same; the lead frit looks like melting at very few grades (5^0C) earlier than the bismuth one. This favorizes the introduction of the proposed frits, the flow sheet allowing the fire on the same diagramme, in the same decorations of the colorants prepared with the considered frits. There are no weight losses and this certifies the chemical stability of the color during firing.

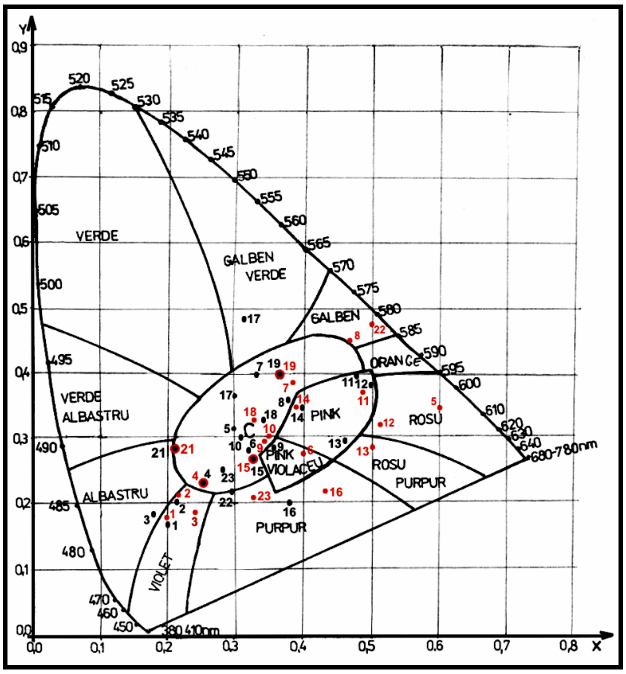

Fig. 9. The place of studied colors in the chromaticity diagram.

Systematic researches were worked out for the study of development of color characteristics, by using in parallel the lead frit (a) and the one experimentally prepared, with bismuth (b), in rigorous, perfectly constant conditions. After firing in industrial furnace, the samples have been put to color determinations. The place of studied colors in the chromaticity diagram is presented in Fig. 9.

For blue, green and pink colors (cobalt chromophores, caught in spinelic networks and in garnets' stable networks), the provided colors are identical or almost identical, with a minor modification of dominant wavelength (for example 1- 4, 9, 10, 11, 13, 14, 15, 19, 21). It can see that the new proposed flux is compatible with most of tested pigments, so it can state that the new proposed silicon-bismuthic flux does not react with pigments having a spinelic network, garnets', rutile's or zirconium's network.

There exist some compositions (for example 5, 8, 22) that are sensitive to fused flux's action, which have significantly changed their color (the case of pigments from cadmium and selenium double sulphide family and non-stabilized oxides as well). The bismuth oxide put to the reduction effect during firing, fundamentally changes the color, the grey component of bismuth superposing over fundamental colors and degrading the chromatic aspect. The darkening of the color and turning to grey tones are result of reduction of metallic oxide (bismuth oxide at metallic bismuth).

4. Conclusions

A large scale of colorants over the bone china glaze has been synthesized, by using the new proposed frit.

The results showed that the proposed bismuth flux corresponds to a large scale of synthetic networks of ceramic pigments, providing bright, stable, resistant and non-noxious colors. For several pigments whose crystalline network is thermally and chemically resistant, the basic flux preserves its properties during melting, having a homogeneous and constant index of refraction (1.55 at bismuth oxide frit, similarly to lead oxide frit).

The studied composition is not compatible with a restrained family of ceramic pigments that are sensitive to solubilization actions or chemical interactions at 750-800^{0}C temperatures (the case of pigments from cadmium-sulphur, cadmium-selenium-sulphur family and non-stabilized oxides as well).

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