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CHEMICAL STABILITY OF OXIDE OVERGLAZE FILMS

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Overglaze oxide films on ceramics experience the corrosive action of aggressive products in service of their parts. A set of optical methods of study is suggested for a quantitative characteristic of the preservation and aesthetic properties of the surface.

Thin overglaze films, called lusters by Bronyar, have been known since the ancient Greeks and Romans. Judging by the dark fracture of the structure and the presence of hydration water in it, the ancient articles were roasted in a reducing medium at a relatively low temperature, and therefore the decorative effect of such articles is explainable by the near-surface reduction of some metal oxides contained in the easily softening glaze to the free metals or to lower oxidation degrees. Decorated Spanish–Moorish ceramics were coated with a special composition deposited on the already glazed ceramic articles, which provided an unusual luster with a pearly, golden, or purple hue after the reducing roasting.

A new decorative motive is present in luster coatings on Italian majolica, but the palette of lustrous coatings on the faience and porcelain is especially rich. "Metallic" lustrous dies based on preparations that formed glittering noble gloss-metals (for example, tetrachloroaurates) had been obtained by means of oxidative muffle roasting, and ether solutions of many abietates (Brianshon, Schwarz) and phenates (Kaiser) formed a no less expressive oxide film under the same roasting conditions.

Modification of the surfaces of vitreous layers (glazes and enamels) has a long history and has been used for providing an exceptional decorative effect due to the interference of the incident rays of light and the rays reflected from the lustrous surface [1]; this effect is important in modern engineering also [2]. Thin films formed on devitrified glasses, high-density ceramics (including textured ones, for example, obtained by the method of hot pressing), and single crystals are being used successfully in the technology of integrated circuits [3], in fabrication of photomasks and sensitive elements, in optics, etc. The advancements made in techniques for the creation of thin-film materials that make it possible to speak about the nanotechnology in some cases have proceeded in parallel with the development of methods for studying the morphology, the composition, the microstructure, and other properties of the surface [4 – 6].

I have established that lustrous layers often appear on their own on fireclay and dinas refractories in furnaces for roasting technical ceramics that contain volatile oxides (PbO, V_2O_5, etc.). Refractories with an effect of pseudochromatism can be self-glazed in furnaces for melting glass of various compositions emitting volatile corrosives, especially in the case of a periodic decrease in the oxidation potential of the furnace atmosphere.

I have worked on widening the available range of lustrous coatings for known and new [7] glazes on porcelain and faience and noticed that reliable data on the chemical stability of overglaze oxide films are very scarce [8]. Russia does not possess official methodological recommendations for the study of decorated glazed ceramic articles that contact edibles.

This led me to study films from vanadium, bismuth, iron, cobalt, and titanium oxides. The lustrous compositions were represented by solutions of acetylacetonates or abietates of the mentioned metals in 1,4-dioxane with an additive of colophony. The substrates were faience specimens coated with an opacified white boron-zirconium glaze.

The liquid lustrous dies were predominantly deposited by the method of aerography. The optimum temperatures and lengths of the decorative roasting in an oxidizing medium were determined by the values of T_g and T_f of the glaze with allowance for the data of a thermogravimetric study (with the help of an MOM derivatograph) of the processes of pyrolysis of the respective precursor.

In order to imitate the most aggressive components of foodstuffs, we chose aqueous solutions of citric, acetic, and oxalic acids and a solution of sodium carbonate. Corrosion studies were performed for specimens with an area of decorated surface equal to 2 cm^2 partially immersed into 1-liter solutions of corrosives at a temperature of 20°C. In order to control the dynamics of the process, the specimens were suc-

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cessively withdrawn from the solution, washed by water, dried, and investigated by an optical method; the exposure in the solution was for 6 h and 1, 4, and 10 days.

The thickness of the film was controlled in an ÉM-3 laser ellipsometer. The luster was determined in Abbe and "Jemetr" refractometers (laser-like beam, accuracy $n \pm 0.005$). These devices were used to determine the refractive index, the value of which depends on the wavelength. The quantitative characteristic (the Abbe number ν) is a quantity typical for dispersion, i.e.,

$$\nu = \frac{n_D}{n_F - n_C},$$

where n_D is the monochromatic radiation (the yellow line of Na), $\lambda = 589.3$ nm, n_F is the blue line of hydrogen, $\lambda = 486.1$ nm, and n_C is the red line of hydrogen, $\lambda = 656.3$ nm.

The microstructure of the luster coating in reflected light against the light background under normal and side illumination was examined visually with the help of an MVT-71 microscope with a maximum 410-fold magnification.

The data of the tests performed are generalized in Table 1. All the oxide films had an initial thickness of 800 – 1000 nm. Anatase (TiO_2) films have the highest chemical stability. The coating is characterized by a very decorative luster with a pearly hue. The etching rates in all the aggressive media are virtually zero, which is confirmed in principle by the data on the corrosion resistance of titanium-bearing coatings (for example, kitchenware enamel). It is obvious that the chemical stability is preserved in thin films also.

A film of Bi_2O_3 having a pearly hue on white glaze is less resistant to acids, especially to the oxalic one. The film virtually disappears on the second day. Soda exerts the least aggressive action on the coatings. The kinetics of the process indicates that with time (after a longer hold) the surface can become passivated due to the formation of difficultly soluble bismuth. It can be that one of the ways of elevating the chemical resistance of bismuth oxide coatings is to widen the contact layer at a respective increase in the roasting temperature. However, this should affect the color of the coating; the latter will acquire undesirable yellow hues, which will worsen the decorative effect.

A V_2O_5 film (golden lemon hue) is less acid-resistant than a TiO_2 film. The pickling rate in the initial stage is higher in oxalic acid and is hardly observed in the citric and acetic acids. The acid nature of this oxide is confirmed by its behavior in the solution of sodium carbonate.

The chemical stabilities of films from Fe_2O_3 (orange-red hue) and CoO (dark steel-gray color with a khaki hue) are very much alike. These films are intensely pickled by oxalic acid and are resistant to acetic and citric acids. The soda solution is quite aggressive with respect to the cobalt oxide film, which seems to be explainable by the well-manifested amphoteric nature of CoO.

TABLE 1. Data of an Optical Study of the Chemical Stability of Oxide Films

Oxide films	Mean initial pickling rate, nm/day	Abbe number*	Luster,* %
	In a medium of citric acid		
V_2O_5	1.8	33/36	85/84
Bi_2O_3	640	33/70	82/23
Fe_2O_3	21.0	24/25	93/83
CoO	1.5	55/57	79/77
TiO_2	0	33/36	87/84
	In a medium of acetic acid		
V_2O_5	2.5	33/38	85/80
Bi_2O_3	620	34/71	83/23
Fe_2O_3	4.2	23/26	92/90
CoO	4.3	55/56	78/75
TiO_2	0	36/39	87/86
	In a medium of oxalic acid		
V_2O_5	21	34/37	85/80
Bi_2O_3	650	32/71	83/15
Fe_2O_3	110	22/72	94/18
CoO	95	55/70	76/18
TiO_2	0.1	36/34	86/82
	In a sodium carbonate medium		
V_2O_5	1.8	34/36	85/82
Bi_2O_3	1.0	31/33	84/80
Fe_2O_3	0	21/26	93/90
CoO	1.4	54/53	79/77
TiO_2	0	37/36	88/85

* Before the test in the numerators; after 10 days in the denominators.

The refractometric data and the refractive power of luster films confirm the data of the ellipsometry used to calculate the pickling rates of the films.

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