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Oksana Shalygina, Lyuidmyla Bragina and Mykola Kuryakin

POWDER ELECTROSTATIC TECHNOLOGY OF HOUSEHOLD APPLIANCES ENAMELLING

National Technical University "Kharkov Polytechnic Institute"
21, Frunze str., 61002 Kharkiv, Ukraine; shalygina_oksana@ukr.net

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Abstract. Basics and distinctive features of contemporary resource and energy saving technology of powder electrostatic application (POESTA) of vitreous enamel coatings are described. Its technological, economic and ecological advantages over slip enamelling in household appliances manufacture, particularly in Ukraine, are discussed. Synthesis principles of special glass frits with high specific electric resistivity for POESTA and results of investigation concerning development and industrial implementation of ground, direct-on and coloured cover enamels for household appliances are given. Development of compositions for obtaining of easy-to-clean, catalytic and pyrolytic coatings is described.

Keywords: vitreous enamel frits, powder electrostatic application technology, ground enamel, direct-on enamel, chemical resistance, easy-to-clean enamel.

1. Introduction

Vitreous enamel coatings, well-known since antiquity for their use in jewellery, nowadays are widely employed for protection of different metals from corrosion, in particular, at high temperatures and pressure.

Multitude of application fields of enamel coatings is motivated by an outstanding combination of wide variety of technical and decorative properties, *viz*., chemical and thermal durability, water-, abrasion and temperature resistance, mechanical strength, hygiene as well as ability to be coloured with nearly perpetual preservation of colour characteristics. Therefore, in spite of wide use of polymer, metal and composite coatings, the vitreous enamel coatings remain highly demanded and even irreplaceable in certain fields [1].

Evolution of the enamelling industry is closely related to the development and implementation of principally new enamelling technologies. The latter include the technology of coating application in an electric field, particularly electrostatic powder application POESTA. It is used in production of steel enamelled parts of household appliances, water heater tanks, architectural elements, sanitary wares, *etc*.

Large quantities of household electrical and gas appliances, electric water heaters with enamelled parts are manufactured in Ukraine at the present time. The bulk of these products is manufactured by three largest enterprises: Joint Stock Company "Greta" (Druzhkovka Gas Apparatus Plant), "Nord" holding (Donetsk) and "UkrAtlantic" (Odessa). The primary manufacturer and supplier of vitreous enamel frits and powders in Ukraine is Trade-Productive Company "Primex", and main developer of enamel compositions for POESTA is Chair of Technology of Ceramics, Refractories, Glass and Enamels, National Technical University "Kharkov Polytechnic Institute" [2].

Effective cooperation of the manufacturers of enamelled products, enamel frits and powders, consolidated by Ukrainian Enamellers Association, makes it possible the quickly respond to changing trends in the global market, legal and regulatory framework, and prices of raw materials and metals.

1.1. Fundamental Bases of Powder Electrostatic Technology POESTA

Electrostatic application of coatings is based on the transfer of the electric charge to the particles of dry powder. For vitreous enamel powders the method of charging is applied – by corona discharge in electric field. The high voltage of 80–100 kV is provided to charging electrodes of spray-gun in corona discharge charging systems and between the sprayer and grounded steel part the strong electric field is created (Fig. 1) [3].

In corona discharge charging systems negative polarity of charging electrode is used. Electric field strength reaches its maximal value at the end of charging electrode and at a determined level the corona discharge takes place here. Corona discharge is a type of cold plasma. At the corona field free electrons appear which fill the space between sprayer and the part. These electrons bond with molecules-constituents of air to form negative ions. If the electric field beyond corona discharge has sufficient strength the ions will bond to powder particles as they are sprayed.

Enamel particles dispersed by air current and taking negative charge due to the presence of negative ions in the volume (corona discharge product) under the influence of aerodynamic F_p and electric F_e forces are directed to the surface of the part (anode). The force of the resistance of the medium F_s and gravity F_g are counteracting with these forces (Fig. 2).

Electrostatic force F_e acting in electric field with field strength E on charged particle with charge Q equals: $F_e = Q \cdot E$ and is several times greater from the value of gravity F_g, acting on the same particle.

Enamel layer thickness is proportional to voltage, reciprocal to the distance from the spray-gun and depends on fluidity of the powder. Adhesion strength of applied coating to steel part is proportional to the value of powder particles electric resistivity.

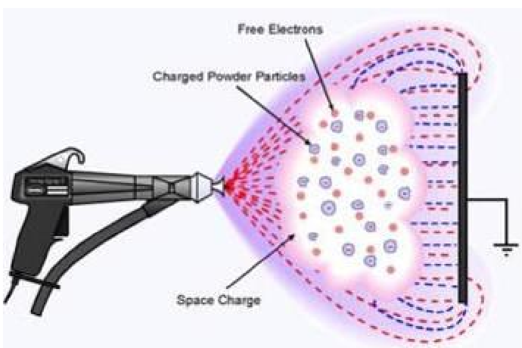

Fig. 1. Charging of particles in corona discharge field

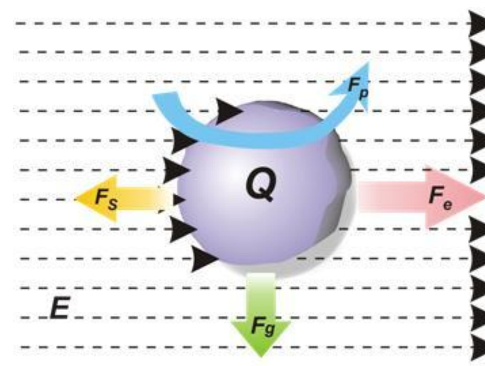

Fig. 2. Forces influencing charged particle in electric field

The success of POESTA technology use depends predominantly on the properties of enamel powder.

2. Experimental

2.1. Synthesis Principles of Vitreous Enamels for POESTA Technology

POESTA technology realization is connected with the use of special vitreous enamel frits having a complex of properties that provides the possibility of fine-sized vitreous enamel powders application in the high voltage field. These properties are high value of specific electric resistivity, definite particle size, fluidity of the powder, and adhesion to steel surface.

While developing the composition of frits we were guided by the following requirements to the powders [4]:

- specific electric resistance of fine-sized powder $\rho_v \geq 10^{11}$ Ω·m;
- own specific electric resistance of enamel frit $\rho_v \geq 10^8$ Ω·m;
- milling dispersity – from 3 to 60 μm, and fraction less than 10 μm must not exceed 5 %;
- fluidity – 90–150 g/30 s;
- adhesion of powder to steel substrate > 75 %.

These requirements, conditioned by the features of POESTA technology, are relevant for all types of vitreous enamel powders, independently from the type and purpose of enamelled products. Service characteristics of obtained vitreous enamel coatings are determined by the properties of initial frit.

Complexity of synthesis of enamels for POESTA technology consists in the necessity to combine simultaneously high values of specific electroresistivity of frits and chemical durability of coatings with their ready fusibility.

As the main idea of this work the following statement was adopted. Obtainment of high specific resistivity and chemical durability of silicate glasses with preservation of their ready fusibility is possible by provision of both polyalkaline effect by simultaneous presence of several kinds of alkaline cations and polycation effect by incorporation of several kinds of alkaline-earth cations to the composition. On the other hand, high intensity of interaction with steel substrate is needed for low-melting enamels. This can be provided by low-activation character of the conductivity of glass melts in the coating firing temperature interval in combination with high values of specific resistivity ρ_v of respective ground frits at room temperature T_{293}.

2.2. Investigations in the Field of Vitreous Enamels for Household Appliances

2.2.1 Development and industrial implementation of ground, direct-on and coloured cover vitreous enamels compositions for domestic stoves

Direct-on vitreous enamels for stoves, regardless of application technology, must correspond to the following complex of requirements [5]:

- adherence strength to steel substrate 4–5 points according to Ukrainian standards, or ≤3 points according EN 10209;
- chemical durability of class A according to EN 14483-1-9 («stain test» – citric acid);
- colour;
- gloss.

The main obstacle for completion of the given task is the finance aspect, namely that the price of enamel frit by raw materials must be lower than the price of similar special frits in the world market. Besides, in connection with adoption of European standards on enamel frits production by Ukrainian enterprises, limitations of fluoride content, Mo, Ba, Zn compounds and nickel oxide (which is the main adherence oxide along with cobalt oxide) must be taken into account in developing of enamel compositions.

Development of the compositions in this case provided obtainment of competitive low-melting ground and direct-on enamels with complex adherence activator (CAA) that contains minimal quantity of valuable adherence oxides NiO and CoO with the fire temperature T = 1073–1113 K.

It needs to be mentioned that the cost of traditional adherence oxides NiO and CoO in ground and direct-on dark-coloured enamels compositions is 45–70 % of the cost of enamel, their total content is 1.5–3 mas %.

Lithium-containing compounds are also expensive components in low-melting enamel compositions for POESTA technology. Their cost may be from 8 up to 16 % of the cost of all raw materials of enamel batch. Introduction of lithium oxide to the frit composition for POESTA provides high electric resistivity, increases wetting ability of the melts and does not decrease chemical durability of coatings. For that reason the possibility of the synthesis of lithium free compositions for POESTA was investigated.

Two main directions of low-melting vitreous enamel frits synthesis were used in the work. The first one is development of high alkaline compositions with content of (Na_2O+K_2O) = 20.0–28.0 mas %; and the second one – obtainment of high boron compositions with B_2O_3 content from 18.0 to 28.0 mas %.

2.2.2. Development of special vitreous enamel compositions for ovens

The search for competitiveness in the field of domestic cooking appliances has instigated the development of new materials and new technologies of synthesis of vitreous enamels with special properties.

One of the most challenging pieces of domestic cooking appliances is oven. Here a major problem is caused by food residues splattered onto the inner walls or other parts of the oven and scorched during cooking process. There are several ways to deal with this problem, including the use of easy-to-clean enamel coatings and self-cleaning coatings (pyrolytic and catalytic) which can be applied by the POESTA technology.

Easy-to-clean (ETC) enamels. Two different types of ETC enamel coatings are known: coatings with nanostructured surface and coatings with very smooth surface [6]. Both types of coatings have high chemical durability (class AA according to EN 14483-1), reduced surface free energy and are defect-free.

Self-cleaning enamels. There are two types of self-cleaning enamel coatings for ovens: pyrolitic and catalytic coatings. The pyrolytic enamel coatings are specially developed enamels capable to withstand temperatures about 773 K, at which the food residues are burned down to ash without combustion. The resulting ash is easily removed from the surface of enamel coating by wiping it with dry cloth. The main drawbacks of the pyrolytic oven are high energy consumption and need for effective thermal insulation. The catalytic coatings allow eliminating of food soils at normal oven operating temperatures (about 523 K) due to catalytic particles present in the vitreous enamel coating and to porous coating structure. Transition metals and their oxides, borides and silicides are commonly used as oxidation catalysts. Acid and activated clays, synthetic and natural zeolites, aluminates and magnesium and aluminium silicates are used as decomposition catalysts. We have found that highly effective catalytic coatings can be obtained by combination of decomposition and oxidation catalysts. By co-melting enamel frit with catalyst and granulating the resulting product, catalytic coatings with complex catalytic filler containing oxidation and decomposition catalysts can be obtained using powder electrostatic application technology. Glass-ceramic coatings with catalytic crystalline phase suitable for this technology are well known.

3. Results and Discussion

3.1. Synthesis Principles of Vitreous Enamels for POESTA Technology

The idea presented for achievement of high specific resistivity and chemical durability of silicate glasses was realized by synthesis of compositions of vitreous enamel frits on the basis of glass matrix in the system R_2O-RO-B_2O_3-SiO_2, where R_2O – Na_2O, Li_2O, K_2O; RO – CaO and BaO, complex adherence activator and modifying additions for increased chemical durability, water and thermal resistance.

Experimentally determined optimal correlation of alkaline and alkaline-earth oxides for obtainment of own specific resistance of glass powders $\rho_{293} \geq 10^{10}$ Ω·m (Fig. 3) was the following (molar units): $2Na_2O$:$1K_2O$:$1Li_2O$ and 1BaO:1CaO.

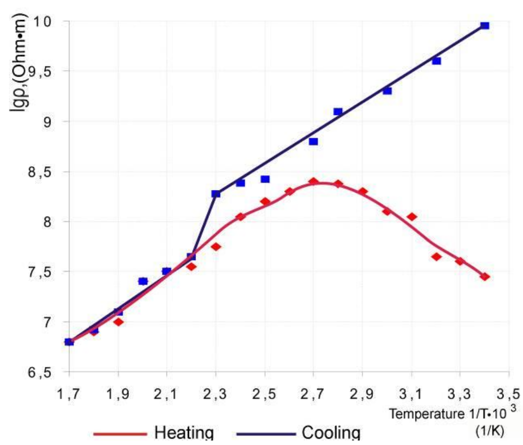

Fig. 3. Temperature dependence of electric resistance of model glass

3.2. Development and Industrial Implementation of Ground, Direct-on and Coloured Cover Vitreous Enamels Compositions for Domestic Stoves

Development of complex adherence activator (CAA) was carried out by sequential introduction of compounds that increase reaction activity of the melt: MnO_2, Fe_2O_3 and CuO. Simultaneously the fusibility of enamel frit was increased with preservation of its high own specific resistivity $\rho \geq 10^9$ Ω·m. This adherence activator was introduced to ground enamel composition with firing temperature of corresponding coating that was T = 1073–1113 K providing intense interaction of vitreous enamel melt with steel substrate and obtainment of protective coating with adherence strength of 4–5 points by the Ukrainian standards, or 1–2 points according to EN 10209.

As a result of investigations, a series of experimental compositions (over 50) of low-melting direct-on dark-coloured vitreous enamels marked as DM was developed. Some compositions of frits of the series, including DM 9, DM 36, DM 39, and DM 40, containing up to 1 mas % of Li_2O and the rest –lithium free ones are provided in the Table 1, where R_2O_3 – B_2O_3+Al_2O_3; R_2O – Na_2O+K_2O+Li_2O; RO – CaO+BaO.

According to the adopted conception, in development of both first and second series of DM compositions polyalkaline and polycation effects were used for provision of high specific electric resistance of 10^8 Ω·m, due to introduction of alkaline oxides Na_2O and K_2O in molar ratios 5:1 and 4:1 and alkaline-earth oxides in molar ratios 2:1 and 3:1.

Table 1

Compositions of experimental frits, mas %

Frit labelling	SiO_2	B_2O_3	Al_2O_3	RO_2	R_2O	RO	Complex Adherence Activator		CaF_2	P_2O_5
							CoO+NiO+CuO	MnO_2+Fe_2O_3		
DM 36[1]	30.9	20.0	–	2.0	26.5	6.0	1.6	5.0	4.0	2.0
DM 39	32.0	19.0	–	2.0	28.0	5.0	1.5	5.0	3.5	4.0
DM 40[1]	32.4	20.0	–	2.0	28.5	5.0	1.6	5.0	3.5	2.0
DM 9	45.0	13.0	–	1.5	23.0	8.0	1.8	3.7	4.0	–
DM 45[1]	43.5	27.0	2.0	–	13.0	5.5	1.5	4.0	3.5	–
DM 48[2]	40.3	17.0	8.0	–	20.0	5.6	1.2	0.6	4.0	–
DM 49[2]	50.3	26.1	2.2	–	12.9	1.1	1.2	1.2	5.0	–
DM 51[2]	48.1	12.0	5.0	–	18.5	10.0	1.2	1.2	4.0	
DM 58[2]	49.5	20.0	3.0	–	14.0	4.0	1.0	4.5	4.0	–
DM 59[1]	49.5	20.0	3.0	–	14.0	4.0	1.3	4.5	3.7	–

Notes: [1] – nickel-free composition; [2] – copper-free composition

Table 2

Values of lgρ_{293} (Ω·m) of experimental frits

	Frit									
	DM 36	DM 39	DM 40	DM 9	DM 45	DM 48	DM 49	DM 51	DM 58	DM 59
lgρ_{293} before heating	7.1	6.8	6.8	5.3	6.6	6.2	5.9	5.1	6.9	7.2
lgρ_{293} after heating	12.3	11.1	11.17	10.0	11.4	9.2	10.55	9.0	11.7	11.6

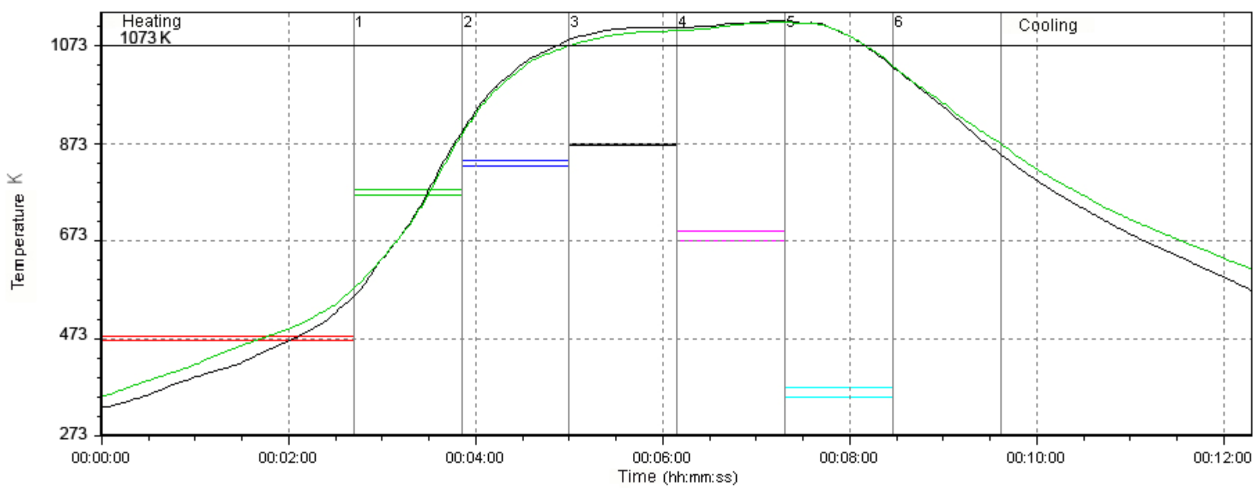

Fig. 4. Temperature-time curve of fire of enamel coatings on parts of household stoves

Frits DM 48 and DM 51, which contain only Na_2O as alkaline oxide, CaO as alkaline-earth oxide, and complex adherence activator not containing CuO and Fe_2O_3 have the lowest values of specific electric resistivity lgρ_{293} ~ 9.0. With the purpose of exclusion of surface conductivity χ_s influence on the resistivity values of glasses its determination was made in the conditions of heating to 473 K – cooling to 293 K. The obtained values of own electric resistivity ρ of fine powders of experimental enamel glass frits after heating to 473 K and cooling to 293 K have confirmed the total influence of polyalkaline and polycation effects (suppression effect) in synthesized compositions on their electric properties (Table 2).

Powders of DM 36, DM 58 and DM 59 frits (without capsulants) showed the greatest values of own electrical resistivity. Powders of these frits capsulated with hydrophobic organosilicon films had electrostatic adhesion to the steel sample A = 85–87 %.

Another major property of direct-on coatings is adherence to the steel base. This value was determined on enamelled samples of low-carbon sheet steel EC-2, fired in the temperature range 1073–1113 K for 4 min. These conditions are determined by the technological features of the equipment and the specifics of the production of enameled parts of household appliances from sheet steel on automated lines (Fig. 4).

Measurements of adherence strength were carried out by impact and by bend tests in accordance with current standards – GOST 24405 and GOST 24788, EN 10209. Results of the determination are shown in Figs. 5-6 and Table 3, where the numerical values and images of the samples are given.

As it is evident from this data, coatings DM 9, DM 36, DM 45, DM 58, and DM 59 were characterized by high adherence strength to EK-2 steel. However, to obtain DM 9 and DM 36 coatings expensive lithium-containing high-boron frits were used. In this case, the optimum firing temperature of coating was 1103–1113 K. High-boron coating DM 45 is characterized by the presence of pores and the lack of gloss. In addition, the coating DM 9 has a bluish tint.

Coatings DM 58 and DM 59 have deep black color and high adherence strength thanks to the use of complex adherence activator (Table 1). This factor, combined with high adhesion degree of powders of these compositions, wide firing interval of the coatings (1073–1113 K), chemical durability of class A (EN 14483-1-9, Ukrainian standards) and the lowest frits cost determined their choice for industrial use in the manufacture of domestic ranges at JSC “Greta” and holding “Nord”. [7, 8]

Development of ground enamels and light coloured cover enamels, implemented earlier on JSC “Azovmash” also relates to investigations carried out in NTU “KhPI”.

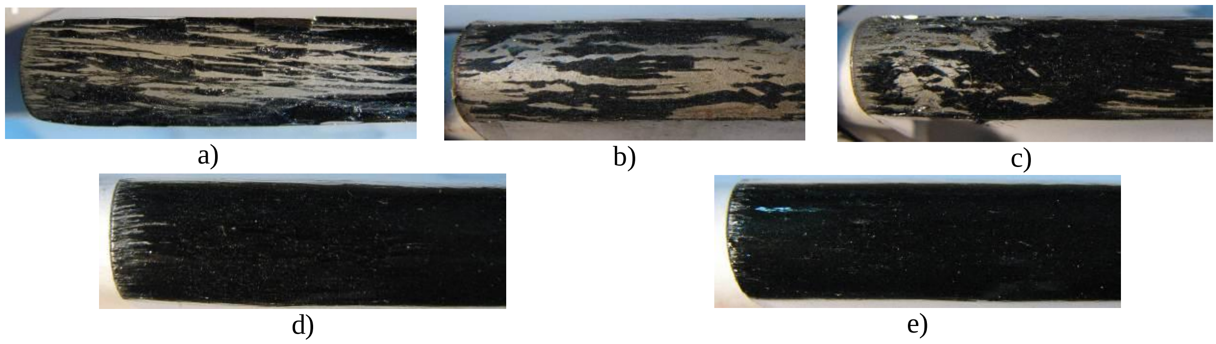

Fig. 5. Adherence strength of coatings (bend test): DM 39 (a); DM 40 (b); DM 48, DM 49 (c); DM 58 (d) and DM 9, DM 59 (e)

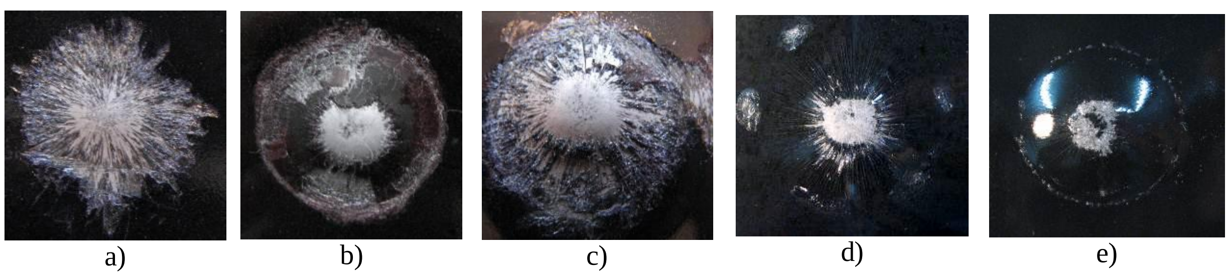

Fig. 6. Adherence strength of coatings (impact test): DM 39 (a); DM 40 (b); DM 48, DM 49 (c); DM 58 (d) and DM 9, DM 59 (e)

Table 3

Adherence strength of experimental coatings to EK-2 steel

Adherence strength of the coatings	Compositions marking									
	DM 36	DM 39	DM 40	DM 9	DM 45	DM 48	DM 49	DM 51	DM 58	DM 59
Impact test, points GOST 24405	4–5	4	3–4	4–5	4–5	3–4	3–4	3–4	4–5	4–5
Impact test, points EN 10209	1–2	3	2–3	1–2	1–2	2–3	2–3	2–3	1–2	1–2
Bend test, points GOST 24788	4–5	4	3–4	4–5	4–5	3–4	3–4	3–4	4–5	4–5

Table 4

Characteristics of ETC-enamels

Coatings	Determination coefficient R^2	Surface free energy			Chemical durability (EN 14483-1-9)	Plum jam test results	
		Dispersive component σ_S^P, J/m²	Polar component σ_S^D, J/m²	σ_S, J/m²		Olive oil	Plum jam
SPG	0.8951	28.11	21.8	49.90	AA	5	5
SAP	0.8628	28.98	21.73	50.71	AA	4	4
SP	0.8360	29.19	21.06	50.25	A	5	4
CE	0.8495	35.21	19.48	54.70	AA	5	5
MO	0.8858	30.36	21.39	51.75	AA	4	5

3.3. Development of Special Vitreous Enamel Compositions for Ovens

In order to compare the cleaning ease of nanostructured ETC-enamel coatings, we have developed coatings of five known classes, *viz.*, CeO_2-containing (CE), silico-alumino-phosphate (SAP) and MoO_3-containing (MO) one-frit coatings, as well as those based on both phosphate and silicate frits (SP and SPG). For easy-to-clean enamel coatings the surface free energy, chemical durability and cleaning ease have been estimated. The surface free energy was measured using Owens-Wendt-Rable-Kaelble method, based on Young's and Good's equations. The test liquids used in these measurements were distilled water, toluene, ethylene glycol, glycerol, formamide, chloroform, methyl benzoate, and benzyl alcohol. The results are given in Table 4.

The cleaning ease was estimated by the Plum jam test [9], which consists in applying food such as plum jam and olive oil on the surface of coated specimen and treating it at 523 K for 30 min. The specimens with burned food soils are then soaked in detergent solution and cleaned (Fig. 7). The cleaning ease is rated by 5 point scale with 5 corresponding to the easiest cleaning. The results of the test are also given in Table 4.

We have found that chemically durable ETC enamels have lower free surface energy and higher chemical durability in comparison with conventional enamels used in ovens, which improve the cleaning ease of their surface.

a) b)

Fig. 7. Easy-to-clean SPG type enamel: after heat treatment (a) and after cleaning (b)

To obtain composite catalytic coating, wollastonite was used as decomposition catalyst because of its catalytic activity and manganese oxide was used as oxidation catalyst. After initial self-cleaning ability tests, the compositions of coatings were chosen. The highest porosity of 17.3 % and self-cleaning ability of 18 cycles according to ISO 8291:1986, were found at firing temperature of 933 K. The resulting compositions of coatings have been patented [10].

4. Conclusions

Principles of vitreous enamels synthesis for obtainment of ground and direct-on coatings for POESTA technology have been devised. Competitive low-melting glass frits for application by the indicated technology of chemically and thermally resistant coatings for protection of steel parts of gas and electric stoves have been obtained and implemented. Competitiveness of the created coatings and the coatings under development due to exclusion of expensive raw materials is shown. Development of compositions for obtaining of easy-to-clean, catalytic and pyrolytic coatings is described.

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ПОРОШКОВА ЕЛЕКТРОСТАТИЧНА ТЕХНОЛОГІЯ ЕМАЛЮВАННЯ ПОБУТОВОЇ ТЕХНІКИ

Анотація. *Описані основи та особливості сучасної ресурсо- і енергозберігаючої технології порошкового електростатичного нанесення (POESTA – powder electrostatic application) склоемалевих покриттів. Обговорюються її технологічні, економічні та екологічні переваги у порівнянні із шлікерним емалюванням при виробництві побутової техніки, зокрема в Україні. Наведено принципи синтезу спеціальних склофрит з високим питомим електричним опором для POESTA і результати досліджень, що стосуються розроблення та промислового впровадження ґрунтових, безґрунтових і кольорових емалей для побутової техніки. Описується розроблення складів для отримання легкоочисних, каталітичних і піролітичних покриттів.*

Ключові слова: *склоемалеві фрити, технологія порошкового електростатичного нанесення, ґрунтова емаль, безґрунтова емаль, хімічна стійкість, легкоочисні емалі.*