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COATINGS

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GLASS-ENAMEL CORROSION-RESISTANT COATINGS FOR STEEL PIPELINES

A. V. Ryabova,[1, 2] **E. A. Yatsenko,**[1] **V. V. Khoroshavina,**[1] **and L. V. Klimova**[1]

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The problem of obtaining defect-free, corrosion-resistant, glass-enamel coatings for steel pipelines is now high-priority. The composition of a corrosion-resistant coating for steel pipes has been developed and the technical and operational properties of the synthesized glass-enamel coatings investigated. The compositions developed for enamel coatings exhibit high adhesion and chemical resistance to corrosive media and can be recommended for use in the production of enameled pipes.

Key words: glass-enamel single-layer coating, enamels for steel pipelines, corrosion-resistant coatings.

A significant drawback of steel pipes is their susceptibility to corrosion, which leads to enormous waste of metal and reduction of pipeline life and increases the roughness of the inner surface of pipe walls with the attendant additional energy consumption on supplying different liquids. Thus, the corrosion of pipes increases both the construction and operating expenses in transportation systems. All this determines the importance of the problem of protecting metal, specifically, pipelines, from corrosion.

One way to solve this problem is to protect steel pipelines by means of anti-corrosion glass-enamel coatings. Because anti-corrosion glass-enamel coatings have adequate strength and universal anti-corrosion properties enameled pipes can be used in practically all industries. Glass-enamel coatings effectively protect pipelines and pumps operating in corrosive environments, hoppers, and water supply and sanitation systems as well as in pipelines transporting industrial wastewater, oil, and so on.

Due to their high hardness and abrasion resistance enameled pipes can be used to transport slurries containing a large amounts of abrasive particles. Pipes coated with glass enamels have a smooth polished surface, which greatly improves pipe performance (hydrodynamic indicators and efficiency). Materials with high adhesion (paraffin) do not stick to enamel coatings. All these qualities and low cost make glass-enamel coatings efficient and cost-effective for protecting pipes.

There exist many glass-enamel coatings that meet the requirements of protection for pipeline with an inner coating. However, despite all their advantages these coatings have some significant drawbacks. The production and use of enameled pipe is energy-consumptive, because it is difficult to obtain a high-quality defect-free glass-enamel coating in a single layer. To obtain competitive enameled products it is necessary to use technologies that reduce energy consumption and production costs by optimizing the production process.

Even though definite advancements have been made in this field the technology for obtaining single-layer enamel coatings for pipelines with stable technological properties and technical-operational performance, specifically, high corrosion resistance to different types of reagents is difficult to implement under industrial conditions. This is due to the complexity of applying and forming a defect-free single-layer coating as well as combining adhesion strength of the primer enamel and chemical resistance of the cover enamel in the single-layer enameling technology.

The purpose of the present investigation was to obtain and improve the performance of corrosion-resistant, single-layer, glass-enamel coatings for steel pipes.

As a result of an analysis of the published data glass-enamel frit with compositions in the glassy system K_2O–Na_2O–Li_2O–CaO–CuO–MnO–Al_3O_3–B_2O_3–CoO–NiO–TiO_2–SiO_2–F were studied. The composition of enamel for steel pipes can be represented in a generalized way as fol-

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[1] M. I. Platov South-Russia State Polytechnic University (NPI), Novocherkassk, Russia.
[2] E-mail: annet20002006@yandex.ru.

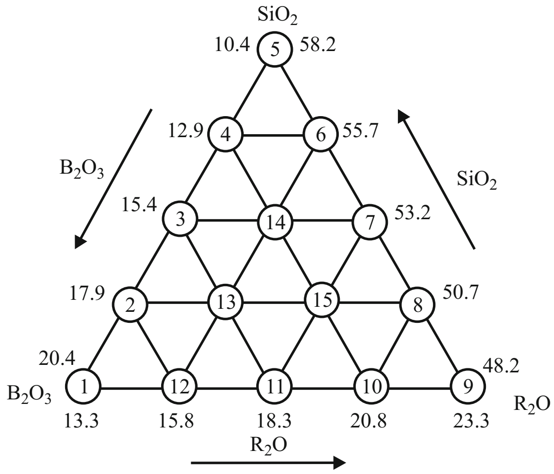

Fig. 1. Range of compositions of the studied glasses (weight content, %).

lows (weight content,[3] %): 48.2 – 58.2 SiO_2; 10.4 – 20.4 B_2O_3; 4.3 Al_2O_3; 13.3 – 23.3 R_2O; 5.8 TiO_2; 2.3 MnO_2; 0.4 CuO; 6.1 Na_2SiF_6; 1.4 NiO; 1.5 CoO.

The range of compositions of the experimental glass-enamel frits is presented in Fig. 1. Oxides forming a glassy structure were chosen as the variable components: SiO_2, B_2O_3, and R_2O, whose total weight content equals 81.9%. The content of other oxides was fixed at a single level and remained unchanged.

Fifteen glass matrices were synthesized on the basis of this diagram. The initial materials for preparing the raw batches with the prescribed composition in the synthesis of enamels for steel were as follows: Na_2CO_3, $Na_2B_4O_7 \cdot 10H_2O$, KNO_3, KNO_3, $NaNO_3$, analytically pure grade H_3BO_3, ultrapure grade TiO_2, C-070-1 type quartz sand (β-modification of quartz), and PShK 0.15 type native feldspar from the Vishnevogor deposit. Fluorine F was introduced into the batch (in excess of 100%) in the form of sodium silicofluoride Na_2SiF_6 (chemically pure grade).

The raw components were subjected to comminution up to passage through a 05 sieve and mixed in prescribed amounts in a porcelain mortar. Melting was done in chamotte crucibles in an electric furnace at temperature 1280 – 1300°C in 65 – 90 min followed by granulation of the melts in water.

The enamel slips were prepared by milling glass frit in porcelain drums with the addition by weight (in excess of 100%) of 7.0 parts of refractory clay, 0.1 parts each of the electrolytes $NaNO_3$ and KCl, and the required amount of water.

The glass enamels were applied under laboratory conditions by two methods: the slip method on the surface of flat steel samples (08kp type) and pouring on vertically arranged samples in the form of steel stub tubes (32G2F type).

In connection with the special role of the preparation of the metal surface for single-layer enameling prior to application of the enamel the surface of the steel samples was carefully degreased, etched, washed in water and a neutralized solution, and dried. The samples were fired in an electric compartment furnace at temperature 840 – 860°C for 3 – 7 min depending on the thickness of the steel sample.

Analysis of the qualitative characteristics of the enameled samples showed that the enamel coatings containing more than 18.3% of alkali oxides are chemically unstable (class-D according to GOST 24788–2001), since the alkali metal oxides act as fluxes, improving fusibility and lowering, and they increase luster of the enamel. However, they decrease the chemical stability of enamels as well as the strength and hardness.

Samples with B_2O_3 content less than 15.8% are characterized by the presence of a large number of defects in the form of burnouts in the enamel layer. This defect is formed because of the high viscosity and surface tension of the enamel melt firing. At the maximum firing temperature (860°C) burst gas bubbles cannot close by means of melting during short firing times, and the bared metal can be oxidized, which results in the formation of a defect.

As result of the analysis of the investigated coatings two optimal compositions — Nos. 11 and 12 — were selected; these coatings provided high chemical stability (chemical stability class A according to GOST 24788–2001) and they had the lowest number of coating defects. The chemical composition of these enamel coatings is presented in Table 1.

To improve the properties of the enamels Nos. 11 and 12, obtain a defect-free glass-enamel coating, and expand the firing interval into the high-temperature range a decision was made to modify their structure, for which grinding additives consisting of quartz in different states — amorphous (diato-

TABLE 1. Chemical Composition of the Enamel Coatings

Composition No.	Weight content of the components, %										
	SiO_2	B_2O_3	R_2O	TiO_2	MnO_2	CuO	Na_2SiF_6	NiO	CoO	Al_2O_3	Total, %*
11	48.2	15.4	18.3	5.8	2.3	0.4	6.1	1.4	1.5	4.3	103.7
12		17.8	15.8								103.7

Notations: R_2O) Na_2O, K_2O, Li_2O.

* Above 100% — fluorine F.

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[3] Here and below, the weight content, %.

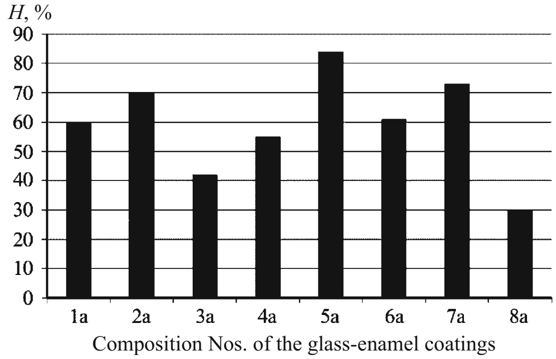

Fig. 2. Determination of enamel – steel bonding strength (bonding index *H*, %) by means of stepwise pulling.

mite) and crystalline (sand) — were used. The main purpose of these additives is to prevent defects due to intense release of gas during the firing of the enamels. Likewise, these additives have a positive effect on the water and acid resistance of a coating. As a result series-a compositions were developed (Table 2).

All enameled samples were tested for chemical stability by the express spot method. This method is intended for testing corrosion resistance of an enamel coating on pipes and shaped details of pipelines. In accordance with the technological specifications a coating must withstand 20% HCl solution for 24 h.

The results of tests for chemical stability showed that the compositions Nos. 1a, 2a, and 4a are most chemically stable and belong to chemical stability class-AA. The composition 3a gives a less resistant coating (class A chemical stability). All other investigated samples belong to chemical stability classes B and C and therefore cannot provide reliable protection of metals.

The series-a synthesized compounds were investigated for the strength of the bonding of enamel with steel by a stepped pulling method. This method of assessment uses stepwise deformation of the test sample to 7 mm in intervals of 1 mm with monitoring of the entire course of fracturing of a coating, starting from the moment of the appearance of the first surface split-off, indirectly characterizing the cohesion of the material, up to complete failure of the material and the bonding layer. The results of the strength measurements are displayed in Fig. 2.

TABLE 2. Sereis-a Glass Enamel Coatings with Grinding Additives

Composition No.	Weight content, %			
	sand	diatomite	frits	
			Composition No. 11	Composition No. 12
1a	–	10	90	–
2a	10	–	90	–
3a	20	–	80	–
4a	–	20	80	–
5a	10	–	–	90
6a	20	–	–	80
7a	–	10	–	90
8a	–	20	–	80

Analysis of glass-enamels showed that the samples with the compositions Nos. 2a, 5a, and 7a exhibit high bonding strength; split-offs and damage to the coatings are not observed. However, the compositions Nos. 5a and 7a are characterized by low chemical stability. Likewise, it should be noted that the samples Nos. 7a and 8a, containing diatomite, have large numbers of defects in the enamel layer, mainly separation of the coating.

As a result of an analysis of the indicated series of glass enamels the sample No. 2a, having the optimal combination of chemical stability and bonding strength, was picked in subsequent studies. Microscopic analysis was performed in order to study the structure of this coating. Photomicrographs of the coating are displayed in Fig. 3.

As a result it was determined that the thickness of the enameled layer is 250 – 300 μm, and gaseous inclusions of different sizes ranging from 5 to 90 μm were found in the layer of enamel. However, they are much smaller than the total thickness of the enamel layer, they are located in the bulk of the enamel, and they come into contact with its surface so that they do not degrade the quality of the coating. It should be noted that the distribution of the pores over the volume of the coating is nonuniform. Likewise, inclusions with irregular shape are observed in the structure of the enamel.

An energy-dispersive analysis was performed to study the chemical composition of the structural nonuniformities in

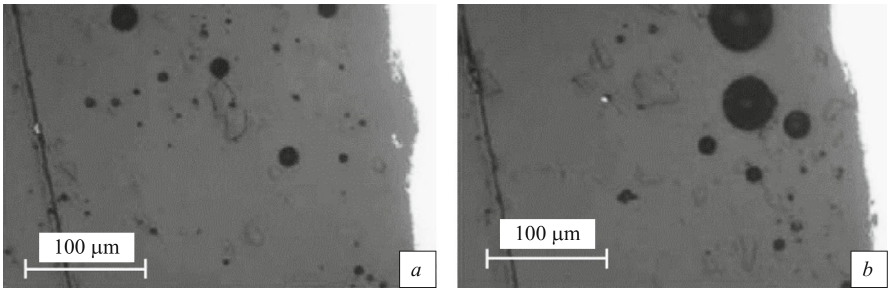

Fig. 3. Appearance of the transverse cross section of enamel No. 2a in different sections of the enameled sample.

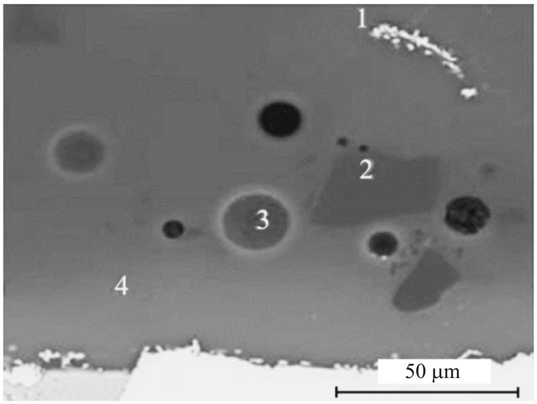

Fig. 4. Appearance of a transverse section of an enamel coating with the composition No. 2a.

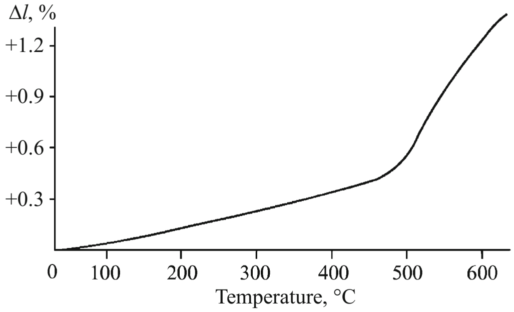

Fig. 5. Relative elongation Δ*l* of the enamel coating No. 2a versus temperature.

a transverse section of the enamel coating (Fig. 4). The results are presented Table 3.

The studies showed (Fig. 4, Table 3) that the composition of the enamel layer is not uniform. Zone 1 is the main glass-enamel mass. The inclusions 2 are SiO_2, probably undissolved grains of sand. The inclusions 3 are a gas phase, as the significant amount of CO_2 evidences. The gas inclusions are always present in the enamel layer, and if they are uniformly distributed over the volume of the coating, then they even improve the elasticity of the layer [1]. Zone 4 is represented by a significant amount of Fe_2O_3 and SiO_2, and it is a transitional layer to the steel – enamel system, imparting strong cohesion. Analysis of the results established that the presence of these inhomogeneities in the volume of the enamel does not degrade the characteristics of the coating itself.

Subsequent studies were conducted to determine the linear thermal expansion coefficient (CLTE) of the synthesized enamel coatings. Thermal expansion is one of the most important properties of enamel, since strong bonding of enamel and metal can be obtained only if their CLTEs are sufficiently close to one another. For this reason, in the synthesis of the enamel the ratio of the components must be picked so that the enamel CLTE is not much less than the metal CLTE, since the compressive strength of the enamel is about 15 – 20 times greater than the tensile strength, so that to obtain a high-quality coating the enamel must be compressed. The enamel CLTE of the coating with composition No. 2a was determined using a vertical quartz dilatometer. The results of the analysis are displayed in Fig. 5.

TABLE 3. Results of Energy-Dispersive Analysis of Enamel Coating with Composition No. 2

Element	Weight content, %			
	Zone 1	Zone 2	Zone 3	Zone 4
Si	24.87	38.99	24.87	24.24
O	48.98	49.36	44.99	42.53
C	–	11.65	18.76	–
Na	6.05	–	6.05	8.61
Al	1.30	–	1.30	0.98
Ca	3.52	–	3.52	3.01
K	1.60	–	1.60	0.62
Ti	4.41	–	4.41	1.90
Fe	9.26	–	9.26	17.99

Analysis of the plot showed that the transition temperature t_g of the enamel equals 490°C, and the CLTE in the temperature range of 30 – 400°C equals $89.4 \times 10^{-7}\ K^{-1}$. This indicates that in terms of the thermal properties this enamel is poorly suited for the steel base because the CLTE equals $(120 - 130) \times 10^{-7}\ K^{-1}$ and the difference in values of the CLTE exceeds the maximum 20%. This is due to the presence of crystalline quartz additive in the investigated enamel and can result in significant degradation of the technical and operational properties of the glass-enamel coating.

To study the phase composition of the enamel with composition No. 2a x-ray phase analysis of the coating was performed.

The investigations have shown that the sample with the glass-enamel composition No. 2a is characterized in the bulk by an amorphous structure but it has a crystalline phase in the form of α-quartz with inter-planar separation 3.34 Å. This is due to the fact that a grinding additive in the form of crystalline quartz, which transformed only partially into an amorphous state during heat treatment, is present in the enamel. As a rule the presence of crystalline phases is undesirable, since an inhomogeneous structure obtains because of it and the properties of the material change [2].

To obtain a defect-free and chemically stable coating with good adhesion to the metal a decision was made to further modify the initially selected compositions Nos. 11 and 12. This was accomplished by combining enamels consisting of two or more frits differing by the spreading, fusion (softening) interval, viscosity, wettability, and corrosion activity.

The compositions Nos. 11 and 12 were picked because the enamel No. 11 contains less B_2O_3 and is more refractory than the composition No. 12, so that the firing interval of the combined enamel expands into the high temperature region.

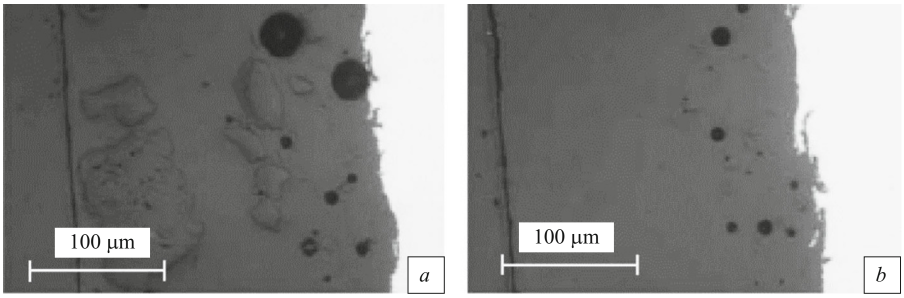

Fig. 6. Appearance of a transvers section of enamel No. 4b on different parts of the enameled sample.

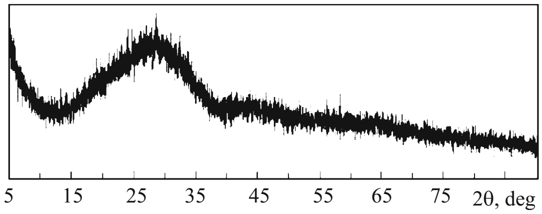

Fig. 7. X-ray diffraction pattern of glass-enamel coating No. 4b.

The enamel No. 12 contains more B_2O_3, and this extends the firing interval into the low-temperature region. The expansion of the firing intervals promotes more complete degassing of the coating and reduction of the size of the gas phase, which has a positive effect on the mechanical properties of the fired enamel coating and also prevents the appearance of different defects.

Glass-enamel slips with series-b composition were prepared in the course of the investigations (Table 4).

The slips were prepared according to the prescribed ratio by wet grinding. The obtained enamel coatings were tested for chemical stability and bonding strength according to GOST 52569–2006. As a result, it was found that only the composition No. 4b possesses high chemical stability and bonding strength, and it forms a defect-free coating. On this basis this composition was picked as optimal for enameling steel pipes.

TABLE 4. Compositions of Series-b Enamels

Composition No.	Weight content, %, of composition	
	No. 11	No. 12
1b	95	5
2b	90	10
3b	85	15
4b	80	20
5b	75	25
6b	70	30
7b	65	35
8b	60	40
9b	55	45
10b	50	50

The structure of this coating was studied by means of microscopic studies of the optimal composition No. 4b. Photomicrographs of a transverse section of glass enamel and steel are displayed in Fig. 6; their analysis has revealed that gaseous inclusions are also present in the bulk of the enamel, but their number and size are, on the whole, much smaller. The maximum diameter of gas inclusions is 2 – 40 μm, and the inclusions are more uniformly distributed in the bulk of the glass-enamel coating. The thickness of the enamel layer shall equals 250 – 300 μm.

Energy-dispersive analysis of the coating with composition No. 4b was also performed.

The studies showed that the coating structure is homogeneous, and this attests completeness of the interaction processes occurring between the grains of frit of the compositions Nos. 11 and12.

x-ray phase analysis of the coating was performed in order to study the phase composition of the enamel No. 4b. The results are displayed in Fig. 7.

The x-ray analysis showed that the glass-enamel coating No. 4b is completely amorphous and does not exhibit any marked peaks. The amorphous homogeneous structure of the coating has a positive effect on the mechanical properties of the coating and its capacity to resist the chemical action of the glass-enamel coating.

Dilatometric studies of the synthesized enamels with the optimal composition No. 4b were also performed (Fig. 8).

The studies revealed that the enamel with the composition No. 4b has a transition temperature t_g equal to 480°C, and the CLTE in the temperature range 30 – 400°C equals 101.9×10^{-7} K^{-1}. The CLTE of this enamel is somewhat greater than that of the previously investigated sample No. 2a containing crystalline quartz as an additive. The difference of the CLTE between steel and the sample does not exceed the admissible value and equals 13.9%. This ratio of the CLTE values ensures that compressive stresses are present in the enamel layer and increase the mechanical strength of the enamel without permitting separation of the coating from the steel base.

The composition No. 4b was picked on the basis of the investigations of the developed series-a and -b compositions. Technical and operational properties of this glass-enamel coating make it possible to use it for reliable protection of the inner surface of steel pipes.

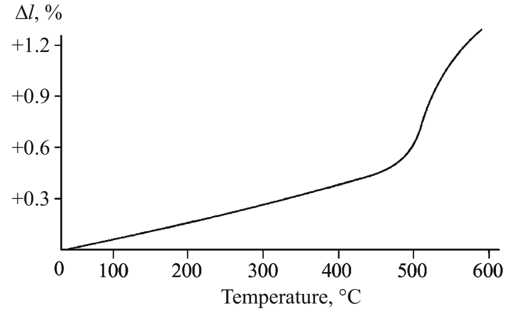

Fig. 8. Relative elongation Δl of the enamel coating No. 4b versus temperature.

Technical and Operational Characteristics of Enamel No. 4b

Spreadability, mm	42.5
CLTE, K^{-1}	101.9×10^{-7}
Coating thickness, μm	250 – 300
Softening point, °C	480
Firing time, min	3 – 4
Firing temperature, °C	840 – 860
Chemical stability class	A
Adhesion index H, %	73.56

The optimal composition of corrosion-resistant glass-enamel coatings for protecting steel pipelines was developed on the basis of these studies, which were performed using of set of physical and chemical methods. The use of this technology in production will significantly lower the production costs of enameled steel pipes as a result of the use of glass frit of single-coat enamel produced in Russia. This will make the products more competitive by reducing the production costs and yielding products with high technical and operational properties.

We have filed an application for a patent in the Russian Federation (No. 2016149705/03(079859)). Industrial testing of enamel coatings for steel pipelines was also conducted based on the industrial base of the Enameled Pipe Plant in Izhevsk.

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