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Novel Nonfluor Corrosion Resistant Coatings Based on Material Resources of Georgia

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Abstract

The possibility of using carbonate manganese ore from Chiatura Deposit (Georgia) in the glass enamels industry is described. The nonfluor multicomponent manganese-containing glasses have been designed. Their chemical stability has been established according to ASTM C650. It is shown, the chemical durability of all glasses to inorganic acid is strongly dependent upon the SiO_2 content in glasses. The kinetic analysis of glass materials corrosion processes was presented. The roughness parameters responsible for deposit growth on investigated surface are analyzed. The optimal glass composition was used to obtain high-quality tracks in the "metal-vitreous enamel" system. Upgraded cost-effective enamel coating may initially provide adequate protection of steel pipes and can be recommended for testing on pipelines.

Keywords

Glass, Enamels, Coatings, Carbonate Manganese Ore, Chemical Resistance, Corrosive Medium

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1. Introduction

Corrosion is the single most costly problem in oil pipelines. No matter how well these pipelines are constructed, once in place they are subjected to severe corrosion effects in service, literally destroying miles of steel pipes annually. The accident and leakage from pipelines cause the region economic and environmental damage. Prevention of corrosion by using rust-resistant coatings, including glass enamel-based materials, can minimize eliminate economic losses and avoid an ecological catastrophe in the region[1-5].

The functional and consumer qualities of enamelled pipes as composite materials of the system "metal-vitreous enamel" are determined by such a property of the initial glass as the chemical resistance regulated by DIN, ISO and ASTM Standarts.

The corrosion resistance of pipe coatings is estimated by the values of weight loss per unit area of their surface (mg/cm^2) in a certain time period.

The leaching kinetics of glasses and vitreous enamels in acid solutions is described by the following equation [6-10]:

$$\Delta m = k\sqrt{\tau} \quad (1)$$

where k is the constant; τ – time.

After leaching, the silica-rich layer has formed on the glass surfaces that caused the dissolution rate to reduce with time. Corrosion of enamel coatings by alkaline solutions in time obeys a linear relationship:

$$\Delta m = b\tau \quad (2)$$

where b is the constant.

Such course of corrosion for glasses and enamels has been confirmed many times [6-10].

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2. Research Significance

As a result of extensive inexpensive quarrying operations and mineral resource imdustry activity in Chiatura region of Georgia a large qvantity of carbonate ore poor in manganese has been accumulated. Utilization of waste is a big problem considering safe disposal, environmental pollution and health hazards. Thus, the problem of waste is daily. It was suitable to utilize it as a raw material to produce anticorrosive glass coatings [9, 11].

In this connection, our objective in this study is to propose competitive nonfluor protective glass coatings for steel pipes, synthesized on the basis of technogenic raw material.

3. Experimental Investigation

To determine the optimal compositions of glasses satisfying the requirements for low-melting vitreous pipe enamels, five series of glasses including 24 compositions were studied. Multicomponent manganese-containing glass compositions were synthesized on the basis of carbonate ore poor in manganese (denoted CMO) from Chiatura Deposit of Georgia.

Carbonate ore belongs to the class of complex materials. It contains materials that are not only compatible but also beneficial and encouraging the incorporation of different types of components and quarry residues in the manufacture of traditional glass materials. Chemical compositions of carbonate ore are shown in Table 1.

Table 1. Chemical analysis of carbonate manganese ore.

Component		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	$\sum(Na_2O+K_2O)$	$\sum(SO_3+TiO_2)$
	1	43.3	8.1	3.1	10.1	2.5	26.8	2.6	3.5
Percent	2	41.1	8.2	2.1	9.1	3.2	32.2	2.4	1.7
	3	53.0	6.0	4.5	12.5	1.4	19.0	2.6	1.0

№ 1 and 2 compositions referred to the industrial and processed to produce manganese dioxide. № 3 composition used in this work contains *MnO* slightly less than № 1 and 2 and richer in silica. This ore composition can be used only in the milled form. The grinded samples were then sieved to required particle size in the range 0.5-1 mm.

The batches were obtained by mixing the grinded waste, the industrial grade quartz, zircon, borax, and soda as raw materials. So the batches of nonfluor glasses are prepared from CMO, sand, borax, zirconium and soda (Table 2).

Table 2. Suggested batches compositions for I-V glass series; (x - 5, 10, 15, 20 wt. %).

Component		CMO	quartz	zircon	borax	soda
	I	30	$50-x$	x	5	15
	II	35	$45-x$	x	5	15
Percent	III	40	$40-x$	x	5	15
	IV	45	$35-x$	x	5	15
	V	50	$30-x$	x	5	15

Glasses are melted at 1300-1350°C for 1.5-2.5 h. After the fusion the melt is quenched in water to get a glass frit.

Coatings are produced by the slip-firing technology on steel test pieces thickness 2.0-10.0 mm precoated with production ground 3132 [7, 9]. The slips were prepared by milling of the frits with additions of clay, electrolytes and water. After drying, the slip layer was fired at 800-820°C. The thickness of coating was gradually heightened and made 0.75-0.80 mm.

4. Analytical Investigation

Basic mixtures (Table 1) do not contain harmful compounds and fluorine and, consequently, all the glass components are non-toxic, related to the environment.

Zirconium oxide was introduced by using the zircon concentrate containing a set of microadditions of f-metal oxides (up to 1.7 wt. %), which exert a favorable effect on the properties of zirconium glasses and enamels [7, 9, 12].

Table 2 shows that five series of glasses were obtained by keeping in each series CMO constant and partial replacement of quartz by zircon from 5 to 20 kg.

Coating quality was estimated both by visual inspection and the method of assessing the strength properties and thermal stability with simultaneous control of covering continuity. Scanning electron microscopy using a JEOL JSM 6380-LV instrument was used to observe the coatings morphology. The roughness parameters of developed enamels were registered on profilograph-profilometer model 252. Corrosion resistance of enameled samples has been tested according to ASTM C650. The chemical stability of glasses was estimated by powde method basis on the total mass losses of glasses in hydrochloric acid. Enamel microstructure was examined by SEM techniques.

5. Comparison of Predictions and Experimental Results

The chemical stability of the sintered glass frits were estimated in hot 20% HCl solution. In these experiments glass powder were exposed for 4 hours in boiling hydrochloric acid. Figure 1 shows the chemical stability of all glasses to inorganic acid is primarily determined by the SiO_2 content in glasses. The tests have shown a good correlation between the increase in corrosion durability and the strengthening of the structural network.

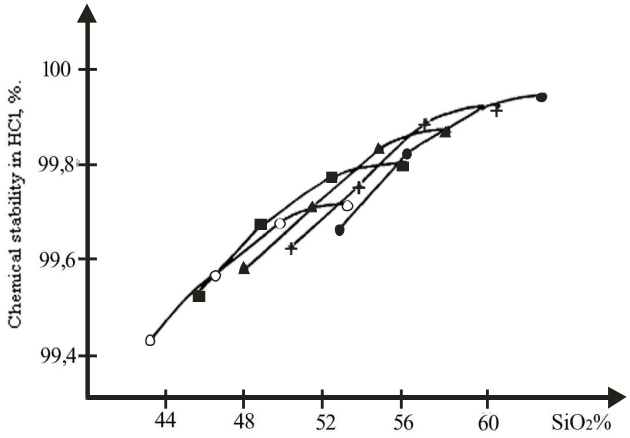

Figure 1. Effect of SiO_2 content on the chemical stability of glasses in hydrochloric acid.

• - I series, + - II series, ▲ - III series, ■- IV series, ○- V series

In Figure 1 it is seen that the best acid resistance (more than 99.8%) of studied glasses is observed when the content of silica in an amount 54.2-62.0 wt. %. Replaicing the sand by carbonate ore causes an increase in the alkali resistance of the frits, but replaicing the SiO_2 by ZrO_2 leads to a similar effect.

Highly resistant to corrosion glass frits are selected and acceptable for synthesis of competitive fluorine-free vitreous enamels for service in oil industry to protect pipes from corrosion. Glass enamels after firing at 800-820°C form qualitative, defect-free, thermomechanical stress-resistant coatings: thermal shock resistance of coatings is 240°C and shock strength – 5-6 J. These are referred as coatings F1, F2, F3 and listed in Table 3.

Table 3. Chemical composition of nonfluor coatings.

Oxides	F1	F2	F3
$SiO_2 + B_2O_3$	66.1	63.7	61.4
$ZrO_2 + TiO_2$	3.4	3.45	3.5
$Fe_2O_3 + Al_2O_3$	3.3	3.8	4.3
$MnO + CaO + MgO$	10.0	11.65	13.25
$Na_2O + K_2O$	17.2	17.4	17.55

Figure 2 shows the scanning electron micrograph of obtained nonfluor enamel coating after firing. The coatings show good homogeneous morphology and completeness structure providing the satisfactory thermal stability of the structure for practical purposes in wide range of temperatures.

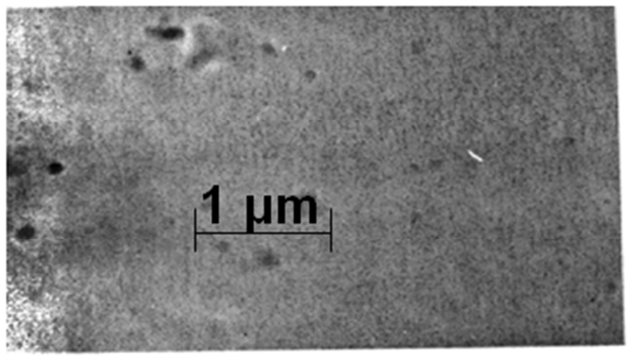

Figure 2. Microstructure of enamel coating F1.

It is known that the selection of enamels for pipelines is done in respect to the aggressivity of transported medium [7, 9, 13, 14], presence of acids, alkali, salts in them. Thus, enameled pipe wall must be resistant to all destructive factors.

Coated samples have been tested for chemical resistivity according to ASTM C650 and Table 4.

Table 4. Chemical test according to ASTM C650.

Corrosive medium	Concentration (%)	Duration (h)	Temperature (°C)
HCl	20	48	15-21
NaOH	5	0.5	60
H_2SO_4	3	16	100

Figure 3 shows the results from the cyclic corrosion tests of coated specimens in boiling 3% H_2SO_4 solution, testing time – 16 hours. The analysis of leaching kinetics of glasses show that course of leaching curves was in good agreement with the equation (1).

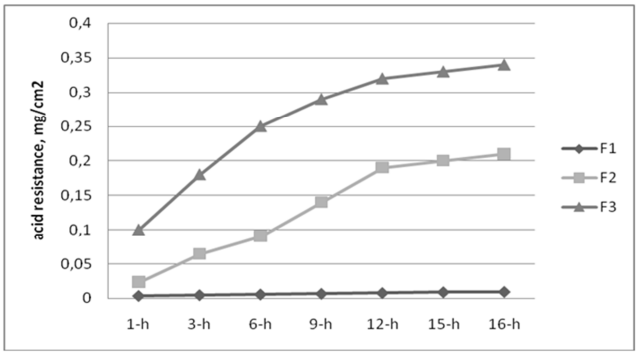

Figure 3. Curves of mass losses of coated specimens in H_2SO_4 solution (ASTM C650).

It was evident that an increase of the silica content in the enamel composition (F1 contains 62.6 wt.% SiO_2, F2 – 60.2 wt. % SiO_2, F3 – 57.69 wt.% SiO_2) increases its acid resistance and reduces the corrosion rate.

6. Discussion of Results

The research results show that chemical resistance of the coating F1 is acceptable for using on inner surface of steel pipelines. Generally, glass enamel has a good resistance to all acids up to a relatively 100°C, except to hydrofluoric acid. Practical experience with coating F1 in inorganic acids has shown that it is highly resistant to this type of environment. Coating F2 undergoes a visible change (mass losses is 0.21 mg/cm^2). The leaching proceeds linearly in the first 12 hours followed by a gradual fall in corrosion rate in the posterior time interval, due to theformation of a passivating silica layer. For coating F3 it was observed significant destruction of surface (mass losses up to 0.34 mg/cm^2).

So, glass coating F1 posess better corrosion protection properties: after exposing the specimen for 16 h in the test acid the surface of coating is glassy and black. The alkali resistance of coating in hot 5% NaOH (60°C) was 0.19-0.3 mg/cm^2. Corrosive losses in 20% HCl solution at 15-21°C for 48 hours are 0.022-0.03 mg/cm^2. Testing according to ASTM C650 constitutes no problem for coating F1.

The corrosion resistance combined with the mechanical properties gives coating F1 good resistance to erosion corrosion. Testing of pipes whose inner surface was protected by developed enamel indicated that coating F1 is resistant to the effect of sand containing aggressive media. The samples are exposed in crude oil for periods of 6 months. After an exposure period visual survey of pipe samples proved that inner surface of pipes was covered with thin layer (0.05-0.1 mm) of mixture of inorganic salts and oil products (tar, wax). Deposited material is easily and quickly removed from the coating F1 test-surface. The color of coating has not changed. The traces of mechanical wear of coating surface have not been observed. Hence, the obtained enamel coating has excellent resistance in corrosive medium and its smooth glasslike surface prevents deposit build up on coated specimens.

The current studies have shown that surface factors directly affect and responsible for the deposit growth on coated surface. From Figure 4 it is clear that surface microprofile demonstrates high smooth characteristics of glass coating F1. We register such roughness parameters as the maximum height of progections and lowest depth of depressions. From these measurements we are able to determine the roughness of investigated surface.

The surface of the ball is covered with rolls, it allows tor the concentration of tension and prolongs the service life buidating the fine irrearities and creating smooth microprofile.

We can conclude that the surface roughness of developed nonfluor enamel, which is the most important geometric parameter, with the degree of 0.05-0.055 μm prevents paraffin wax deposits from hydrocarbon oil on the pipeline walls and doesn't cause blockade and pressure problems in crude oil production and transportation.

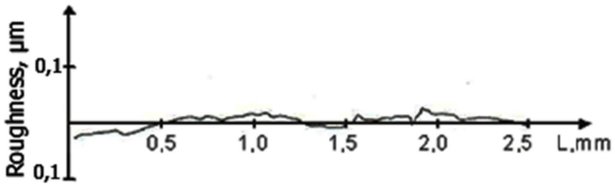

Figure 4. Profilogram of the surface of coating F1.

7. Summary and Conclusions

From the present investigation it can be concluded that synthesized new managanese-containing glass coating is very promising, competitive, contrasting its protective and smoothness characteristics with the cost-effectiveness of the raw material. Farthermore, ecological protective enamel doesn't contain harmful compounds, such as fluorine, BaO, PbO, As_2O_3, and uses less materials since the batche is compiled from 5 components. The obtained glass enamel coating can be used in extreme operating conditionds, where a good corrosion resistance and surface properties are required.

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Biography

Irine Berdzenishvili (1956), female, professor, Ph.D., main research fields: chemical technology of refractory non-metal silicate materials, physical chemistry.