Development of Technology for Anti-corrosion Glass Enamel Coatings for Oil Pipelines

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Abstract. Among anticorrosive coatings for steel products, glass-enamel glass is the most reliable and versatile, based on aluminoborosilicate glasses of the SiO₂·Al₂O₃·B₂O₃·R₂O system. This anti-corrosion coating allows to increase the chemical resistance of the internal surface of pipelines to various groups of reagents. Therefore, in the course of the study, a previously developed composition was modified by introducing oxides SrO, ZrO₂, CaO, MoO₃, Li₂O and their acid and alkalinity of enamel frits and coatings based on them and it was found that the addition of strontium and zirconium oxide in the amount of 2% was optimal.

Keywords: Oil pipelines · Anti-corrosion coatings · Glass-enamel coatings · Steel protection · Chemical resistance · Acid and alkali resistance

1 Introduction

Currently, the oil industry of the Russian Federation is developing rapidly and efficiently. However, corrosion of equipment and facilities in the oil and gas industry is one of the main reasons for reducing their performance, causing huge economic losses and environmental damage. Presently, protective coatings (bitumen, epoxy, polyurethane, etc.) have become widely used to protect oil pipelines, among which glass-enamel coatings with high chemical resistance and thermomechanical properties, in particular, heat resistance, reaching 500 °C, occupy a special place. Due to the fact that the silicate-enamel coating for steel pipelines is exposed to an aggressive environment containing hydrocarbons and formation water, in which chlorides, sulfates and organic acids are present, as well as up to 10% hydrogen sulfide and 10% carbon dioxide. The coating composition was based on an acid-resistant glass composition (Ryabova et al. 2018) with a high content of quartz and low boric anhydride and alkaline oxides, which will improve the chemical resistance of enamels and extend the range of their roasting (Yatsenko et al. 2018).

Also, when choosing the type of protective coating, the following factors should be taken into account: operating conditions, composition of the transported medium, temperature and pressure in the system, speed and nature of the flow movement, presence of abrasive particles in the fluid flow, composition and properties of associated petroleum gas (APG), presence of asphalt-resin-paraffin deposits (AFS), the manifestation of the life of microorganisms.
Therefore, the purpose of these studies was the development of anticorrosive glass-enamel coatings to protect steel pipelines from medium carbon steel 32G2S and the study of factors affecting the process of their defect-free formation and technical and operational properties.

2 Methods and Approaches

The technology of enameling the internal surface of pipelines includes the following technological stages: preliminary annealing of steel pipes at a temperature of ~750 °C in order to remove contaminants and decarburize the outer layers of steel; mechanical preparation of the inner surface of pipes using shot blasting using single or multiple shot blasting units to remove scale and roughen for better adhesion to the glass-enamel coating; preparation of enamel slip suspension on the basis of finely ground glass granulate; application of slip suspension on the inner surface of a horizontal pipe by sprinkling using an impeller; drying at a temperature of 100–120 °C and induction roasting at a temperature of 860–880 °C.

The aim of the work was to develop the composition and technology of applying a glass-enamel single-layer coating for medium-carbon steels, which has high rates of chemical and abrasive resistance and is capable of forming a defect-free smooth coating on the steel surface. To solve this problem, the aluminoborosilicate system SiO$_2$-Al$_2$O$_3$-B$_2$O$_3$-R$_2$O was chosen as the most acceptable in the single-layer enamelling technology, which was modified by introducing compounds such as SrO, ZrO$_2$, CaO, MoO$_3$, Li$_2$O, in order to improve chemical resistance and defect-free formation in the form of through pores. The introduction of enamels strontium, calcium and zirconium oxides that are insoluble in oxides helps to reduce the leaching of alkali and alkaline earth cations when exposed to acid coating. Lithium oxide together introduced with oxides of sodium and potassium contributes to the chemical resistance of enamel coatings due to the manifestation of polyalkalnochnogo and polycationic effects. The amount of additives introduced into the charge was 2 wt.%, Since the introduction of additives less than 1% slightly affects the properties of enamel coatings, and more than 2% can greatly affect the change in the technological properties of the melt.

Next, the compounded mixtures were boiled at a temperature of 1350 °C for 1 h in an electric oven in alundum crucibles, subjected to wet granulation and applied in the form of finely ground enamel slip to samples of 32G2S steel. After drying and firing at a temperature of 850 °C, the resulting enamel coatings were tested to study the effect of modifying oxides on the structure and properties of enamels.

To assess the corrosion resistance, tests were carried out to determine the acid resistance characterized by weight loss after exposure to 20% boiling hydrochloric acid and alkali resistance - weight loss after exposure to 8% sodium hydroxide solution. For frits, the tests were carried out by the grain method, and for enamel coatings, the impact on their surface.
3 Results and Discussion

For the developed modified frits and enamel coatings, chemical resistance to various groups of reagents for weight loss after boiling in acid and alkaline solutions was studied. The test results are presented in Table 1.

Table 1. Indicators of the properties of modified frits and enamel coatings depending on the composition

| Name of enamel | Modifying additive | Chemical resistance |
|----------------|--------------------|---------------------|
|                |                    |                     |
|                |        Frites, %   | Coatings, mg/cm²   |
|                | 20%-HCl  | 8%-NaOH | 20%-HCl | 8%-NaOH |
| 10-0           | Without additives | 0,38     | 0,83     | 0,22     | 0,78     |
| 10-1           | SrO      | 0,32     | 0,99     | 0,16     | 0,45     |
| 10-2           | ZrO₂     | 0,40     | 1,20     | 0,20     | 0,60     |
| 10-3           | CaO      | 0,38     | 0,75     | 0,21     | 0,63     |
| 10-4           | MoO₃     | 0,54     | 0,98     | 0,22     | 0,68     |
| 10-5           | Li₂O     | 0,42     | 0,87     | 0,23     | 0,63     |

The results obtained allow us to conclude that the introduction of modifying additives into the glass matrix composition has a significant impact on anti-corrosion properties.

For all compositions, the mass loss of frits after boiling is quite significant, since the specific surface of glass powders is much larger than the surface of the burned enamel coating. However, the composition of frits modified by strontium and zirconium oxides is characterized by less mass loss, which is caused by their positive effect on the increase in the packing density of the structural amorphous network, due to the large radius of these ions. Molybdenum oxide has almost no effect on chemical resistance, but it has a positive effect on the continuity of the coating contributing to a smoother formation and the absence of coating defects, due to a decrease in the surface tension of the enamel melt. Calcium oxide in such an amount does not affect the chemical resistance of frits and coatings. Lithium oxide increases chemical resistance and frit and coatings, although it is alkaline in itself, but it has an inhibitory effect due to the presence of several alkali cations (Na₂O and K₂O).

4 Conclusions

As a result of the research, the composition and technology of producing anticorrosive glass-enamel coatings for the internal protection of steel pipelines based on the SiO₂-Al₂O₃-B₂O₃-R₂O aluminoborosilicate system has been developed. The effect of various modifiers of the vitreous matrix on the acid and alkali resistance was studied, and it was found that the strontium and zirconium oxides in an amount of 2% are optimal.
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